

Ambient Air Pollution from Wood Burning of Domestic Heating

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To my late mother Zheng Qimei 献给我的阿妈 郑七妹

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Nomenclature

Symbols	Explanation	Unit
ER	emission ratio	%
F	conversion factor	
M	mass	kg
P	percentage	%
R	correlation coefficient	
Subscripts	Explanation	
amb	ambient	
emi	emission	
bef	before	
beh	behind	
ff	fossil fuel	
levo	levoglucosan	
loc	local	
hw	hardwood	
i	wood type i	
sw	softwood	
totPM	total PM	
wb	wood burning	
WBPM	wood burning PM	
Acronyms	Explanation	
AMS	aerosol mass spectrometers	
AS	Australian Standard	
AE	aethalometer	
BaP	Benzo[a]pyrene	
BC	black carbon	
CM	carbonaceous matter	
CMB	chemical mass balance	
COC	condensable organic compounds	
DR	dilution ratio	
EC	elemental carbon	
EFs	enrichment factors	
EN	Europäische Norm	
EU	European Union	

FA	factor analysis
FF	fossil fuel
GC-MS	Gas chromatography–mass spectrometry
IC-PAD	ion chromatography (IC) coupled with a pulsed amperometric detector (PAD)
LANUV	Landesamt für Natur, Umwelt und Verbraucherschutz
MAAP	Multi-Angle Absorption Photometer
MISKAM	Microscale climatic and dispersion model
NIOSH	The National Institute for Occupational Safety and Health
NS	Norwegian Standard
OM	organic mass, organic matter
OC	organic carbon
PAHs	polycyclic aromatic hydrocarbons (PAHs)
PCA	principal component analysis
PM	particulate matter
PM ₁₀	particulate matter with an aerodynamic diameter of 10 µm or less
PM _{2.5}	particulate matter with an aerodynamic diameter of 2.5 µm or less
PMF	positive matrix factorization
RWC	residential wood combustion
TOR	optical reflectance
US EPA	U.S. Environmental Protection Agency
UV	ultraviolet
VOC	volatile organic compounds
WHO	World health organization
w/w	weight by weight

Abstract

Residential wood burning is an important component of domestic heating in Europe. With the advantage as renewable energy, wood burning has, however, become a general environmental issue due to wood smoke pollution in terms of particulate matter (PM) and PM-bound substances like polycyclic aromatic hydrocarbons (PAHs), black carbon (BC) and organic matter (OM), which are well-known for their negative effects on both environment and human health. This pollution problem is serious especially under inversion weather conditions.

The purpose of this thesis is to quantify the wood burning contribution to ambient PM₁₀ during winter heating periods in a residential area in Dettenhausen, Germany. Firstly, the air quality measurements in this area were carried out by sampling ambient PM samples and measuring gaseous pollutants (CO and NO_x) and black carbon in winter 2013/2014 and winter 2014/2015. PM₁₀ mass concentrations were determined and the filter samples were chemically analyzed in laboratories for PM-bound polycyclic aromatic hydrocarbons and levoglucosan. A certain number of filters was also analyzed for organic carbon (OC) and elemental carbon (EC) content.

Concentrations of these air pollutants give an overview of the pollution situation in this area. The results for PAHs show that the carcinogenic potential of total PAHs is 65 % for both winter periods, with most of daily average benzo[a]pyren (BaP) exceeding the EU annual limit value of 1 ng/m³. Black carbon (BC) was measured for the first time in this area and the daily concentration, respectively diurnal trend, through winter 2014/2015 shows a significant contribution from biomass burning. The PM pollution due to wood smoke could be recognized by the substantial levoglucosan found in all PM samples. Levoglucosan was evaluated through its correlations with PM₁₀ and other pollutants like BaP, BC, and gaseous pollutants (CO and NO_x). However, the contribution from residential wood burning could not be quantified directly from these ambient data. According to the application principle and calculation procedure of using levoglucosan as wood burning tracer, the emission ratios of levoglucosan measured directly at emission sources is required.

Therefore, wood combustion experiments at a wood stove were carried out for the investigation of PM-bound levoglucosan. The sampling was carried out with a dilution technique, which was realized through the application of a dilution tunnel built according to EPA method 5G (US Environmental Protection Agency, 2000). Various parameters, defining as operation, combustion and sampling conditions, were applied to investigate their potential influence on the levoglucosan emission levels. The experiment design included two sampling methods for two types of wood which are commonly used in a residential area Dettenhausen: beech hardwood and spruce softwood.

Firstly, experiments with continuous simultaneous sampling before dilution (hot flue gas) and after dilution (diluted flue gas) were carried out and the comparison of the results proved that a dilution tunnel was necessary to cool down and dilute the hot flue gas, which enabled the condensation of levoglucosan on PM at low temperature and to be collected on filters. The levoglucosan measured behind dilution should be used for the determination of emission ratios since it represents the realistic situation. Therefore, levoglucosan was further investigated by sampling only after dilution for different combustion phases. The results show that levoglucosan was emitted mainly at the burn-up phase and the main-burning phase, irrelevant of airflow settings at the wood stove. The comparison between different experimental parameters revealed that cold-start resulted in a relative high concentration of levoglucosan due to the low combustion temperature, but this influence was only limited to the burn-up phase. The dilution ratio could be regulated between 5 and 10, but it was shown not to have an obvious effect on the measured levoglucosan level. Based on these results, a suitable sampling procedure for levoglucosan was suggested and different emission ratios of levoglucosan were calculated.

By estimating the local wood consumption situation, the calculation of wood burning PM contribution with the levoglucosan tracer method was realized after the derivation of local conversion factors which can correlate the levoglucosan to wood burning PM in ambient air. The ambient concentration of levoglucosan was multiplied by the chosen local conversion factors. The obtained values suggested an average contribution of wood burning to total

ambient PM₁₀ is in the range of 16 to 25 % in winter 2014/2015 in the studied area. The comparison with black carbon data showed that biomass burning black carbon has an average contribution of 30 % to the total black carbon. However, the biomass black carbon fraction cannot be compared directly with the wood burning PM₁₀ fraction calculated from levoglucosan because black carbon and PM₁₀ possess different particle size distributions. A better comparison requires further investigations, which can be one of topics in the future of work.

Kurzfassung

Holzfeuerungen sind ein wichtiger Bestandteil der Haushaltsheizungen in Europa. Mit dem Vorteil als erneuerbare Energie sind Holzfeuerungen jedoch zu einem allgemeinen Umweltproblem geworden, vor allem aufgrund der Feinstaubbelastung und Partikelgebundenen Substanzen wie Polyzyklische Aromatische Kohlenwasserstoffe (PAKs), Ruß (BC) und organische Stoffe (OM), deren negativen Auswirkungen auf die Umwelt und die menschliche Gesundheit schon lange bekannt sind. Besonders unter Inversionswetterbedingungen wird dieser Art der Luftverschmutzung zum Problem in Wohngebieten.

Ziel dieser Arbeit ist es, den Beitrag der Holzfeuerungen zur PM₁₀-Belastung während der Heizperioden im Winter in einem Wohngebiet in Dettenhausen, Deutschland, zu bestimmen. Zuerst wurden Immissionsmessungen in diesem Wohngebiet durchgeführt, indem PM₁₀-Proben aus der Umgebungsluft gesammelt und die Schadstoffe CO, NO_x und Ruß gemessen wurden. Diese Messkampagnen fanden im Winter 2013/2014 und im Winter 2014/2015 statt. Die PM₁₀-Massenkonzentrationen wurden bestimmt und die PAKs und Levoglucosan im gesammelten Feinstaub PM₁₀ analysiert sowie der Gehalt an organischem Kohlenstoff (OC) und elementarem Kohlenstoff (EC) bestimmt.

Die Ergebnisse gaben einen Überblick über die Luftverschmutzung in diesem Wohngebiet. Die Ergebnisse der PAK-Analysen zeigen, dass das kanzerogene Potenzial der PAKs in

beiden Winterperioden 65 % der gesamten PAKs betrug, wobei der größte Teil der täglichen Durchschnittswerte von Benzo[a]pyren den EU-Jahresgrenzwert von 1 ng / m³ überschritt. Zum ersten Mal wurde in diesem Gebiet Ruß (BC) gemessen. Der tägliche Konzentrations- bzw. Tagesverlauf zeigte im Winter 2014/2015 einen großen Beitrag aus Holzverbrennung. Die Feinstaubbelastung durch Holzrauch konnte von dem in allen PM-Proben enthaltenen Levoglucosan erkannt werden. Levoglucosan-Konzentrationen wurden in Bezug auf ihre Korrelationen mit PM₁₀ und anderen Schadstoffen wie BaP, BC und gasförmigen Schadstoffen (CO und NO_x) analysiert. Der Beitrag der Holzfeuerung konnte jedoch anhand dieser Umgebungsdaten nicht direkt quantifiziert werden. Für das Berechnungsverfahren, in dem Levoglucosan als Tracer für die Holzverbrennung dient, sind die Emissionsverhältnisse von Levoglucosan erforderlich, die direkt an Emissionsquellen gemessen werden.

Hierfür wurden an einem Holzofen Verbrennungsversuche zur Untersuchung von PM-gebundenem Levoglucosan durchgeführt. Die Probenahme erfolgte mit einer Verdünnungstechnik, die durch den Einsatz eines Verdünnungstunnels nach der EPA-Methode 5G (US Environmental Protection Agency, 2000) realisiert wurde. Verschiedene Parameter, die als Betriebs-, Verbrennungs- und Probenahmebedingungen definiert wurden, wurden bestimmt, um ihren möglichen Einfluss auf die Levoglucosan-Bildung zu untersuchen. Die Versuchsplanung umfasste zwei Probenahmeverfahren für zwei Holzarten, die üblicherweise in diesem Wohngebiet verwendet wurden: Buchen-Hartholz und Nadelholz. Zunächst wurden Versuche mit gleichzeitigen Probenahmen vor Verdünnung (heißes Rauchgas) und nach Verdünnung (verdünntes Rauchgas) durchgeführt. Diese Versuche ergaben, dass ein Verdünnungstunnel zum Abkühlen und Verdünnen des heißen Rauchgases erforderlich ist, mit dem es bei niedriger Temperatur ermöglicht wird, dass Levoglucosan an PM adsorbiert. Das nach der Verdünnung gemessene Levoglucosan kann zur Bestimmung der Emissionsverhältnisse herangezogen werden, da es die realistische Situation darstellt, die sich bei Austritt der Abgase aus dem Schornstein in die Umgebungsluft ergibt. Daher wurden Levoglucosan-Proben bei den weiteren Versuchen nur nach Verdünnung genommen. Um die Abhängigkeit beim Verbrennungsverlauf zu ermitteln, wurden die Proben von verschiedenen Verbrennungsphasen genommen. Die Ergebnisse zeigen, dass unabhängig von der

Luftstromeinstellung am Holzofen Levoglucosan hauptsächlich in der Anbrenn- und der Hauptbrandphase freigesetzt wird. Der Vergleich verschiedener Versuchsparameter ergab, dass beim Kaltstart aufgrund der niedrigen Verbrennungstemperatur eine relativ hohe Levoglucosan-Konzentration vorkommt, die jedoch nur während der Anbrennphase auftritt. Das Verdünnungsverhältnis konnte zwischen 5 und 10 reguliert werden, zeigte jedoch keinen offensichtlichen Effekt auf die gemessenen Levoglucosan-Konzentration. Basierend auf diesen Ergebnissen wird ein geeignetes Probenahmeverfahren für Levoglucosan vorgeschlagen und unterschiedliche Levoglucosan-Emissionsverhältnisse berechnet.

Die Umgebungskonzentration von Levoglucosan wurde mit einem lokalen Umrechnungsfaktor multipliziert. Mit diesem Wert ergab sich ein Beitrag von 16 bis 25 % der Holzverbrennung am gesamten PM_{10} im Winter 2014/2015 im untersuchten Gebiet. Ein Vergleich mit Black-Carbon-Messdaten zeigte einen Biomasse-Black-Carbon-Anteil am gesamten Black Carbon von im Mittel 30 %. Der Biomasse-Black-Carbon-Anteil kann allerdings nicht direkt mit dem aus Levoglucosan berechneten Holzverbrennungs- PM_{10} -Anteil verglichen werden, da es sich um verschiedene Korngrößenverteilungen handelt. Hierzu wären weitere Untersuchungen erforderlich.

1. Introduction

The forecast of running out of non-renewable fossil fuel (FF) has been causing worldwide pressure in economic and political aspects. Meanwhile, negative environmental impacts from FF are a well-known critical issue. In the past decades, global emissions from energy were at historic high levels and the contribution from FF was continually rising (Le Quéré et al., 2018). Increasing FF price and climate change issues like global warming lead to the change of energy consumption structure, in which the share of renewable energy is continuously increasing as it is considered as a good alternative to reduce FF dependence. All member states of EU are committed to increase the renewable energy sources to 20 % of their energy requirements until 2020 with the purpose of reducing fossil-CO₂ emissions (Directive 2009/28/EC, 2009). Financial incentive also pushed private consumers to substitute renewable energy (mainly biomass) for oil or gas utilization in the residential heating section. For example, wood used as heating resource comprises about 35 % of total primary heating energy use of detached housing in Finland (Villar-Vidal et al., 2014). In Denmark, the number of wood stoves and boilers were doubled over a ten year period due to the same reason (Glasius et al., 2006).

1.1 Wood combustion in domestic heating in Germany

Wood combustion for domestic heating has a long history and has developed into a very popular life mode in European countries especially in Germany. In Germany, there were in total 31 million small combustion systems in 2016, of which individual one-room firing systems like wood stoves and fireplaces took up 38 %, corresponding to about 12 million appliances (Umweltbundesamt, 2018). Depending on the technology, various forms of wood fuels could be used with wood logs as the main fuel for wood stoves. It is reported that the consumption of wood as heating fuel energy in private households rose from 22.0 Mio. m³ in 2005 to 33.9 Mio. m³ in 2010, which reached a share of 53 % in the wood energy sector (Mantau, 2012).

1.2 Particulate matter pollution from wood combustion

Using biomass as renewable energy for domestic heating did relieve the pressure from FF to a certain extent and reduces economic costs for private consumers. But wood burning could cause serious air pollution problem.

Depending on combustion quality, different combustion products are produced from wood combustion in small combustion units (Figure 1) (Struschka, 1993). From manually operated compliances, wood smoke is normally a complex mixture containing various air pollutants, including gaseous pollutants and solid fine particulate matter. Gaseous pollutants are mainly volatile organic compounds (VOC), CO and NO_x, while aerosols consist of salt, soot and condensable organic compounds (COC) (Evans and Milne, 1987; Nussbaumer, 2010). These pollutants are emitted in a large amount especially during incomplete combustion, and particulate matter (PM) is considered as the major pollutant from incomplete wood combustion (Simoneit, 2002). Unpleasant smell of wood smoke is another issue which annoys residents most directly, but cannot be measured easily.

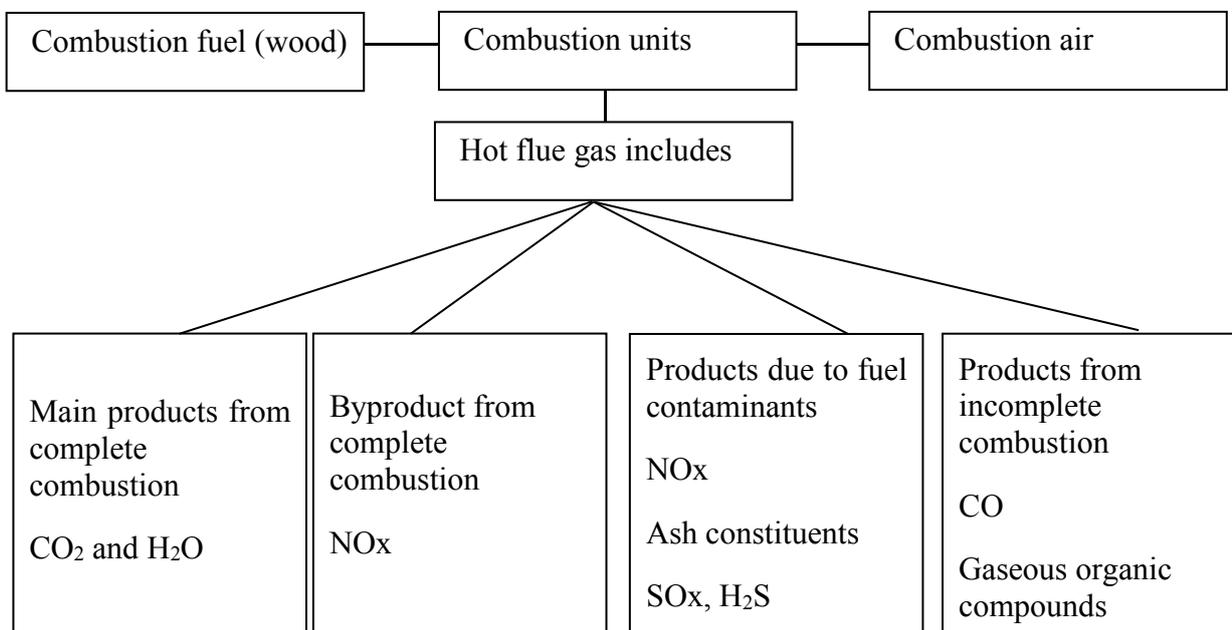


Figure 1: Emission products from wood combustion in small-scale combustion units (Struschka, 1993, p. 59)

Emission level

PM is considered as a prime pollutant responsible for deteriorating ambient air quality and is classified according to its aerodynamic diameter as coarse (PM_{2.5-10}) and fine (PM_{2.5}) particles. PM₁₀ is particulate matter with an aerodynamic diameter of 10 µm or less. In this study, all mentioned ambient PM is referred to PM₁₀, there is no separated discussion about PM_{2.5}.

Besides wood combustion, emissions from vehicular traffic, especially diesel generators, and coal burning in industry and for commercial purposes were found to be other major contributor of PM. However, in the past decades, the share of PM emission from biomass burning was continually increasing and has become one of the predominant contributors. According to the data from the German Environment Agency (Umweltbundesamt; UBA), total PM₁₀ emission in Germany was mainly attributed to industry and traffic, which however decreased gradually due to strict regulation in recent years (Umweltbundesamt, 2019a). In 2016, particulate matter emission (PM₁₀) from the above mentioned 31 million small combustion systems was in total 22.7 thousand tons, in which the emission from wood combustion from wood stoves and fireplaces was responsible for about 87 % of the total emission (Umweltbundesamt, 2019b, Figure 2). Therefore, with the advantage of being CO₂ neutral on one hand, wood used as renewable energy for domestic heating on the other hand causes very high PM pollution as its drawback. Similar situations are also found in other European countries for example in Switzerland (Gianini et al., 2012). This indicates that emission level of PM from wood combustion in domestic heating is significant and comparable to that from traffic emission, which has become a serious local and international issue.

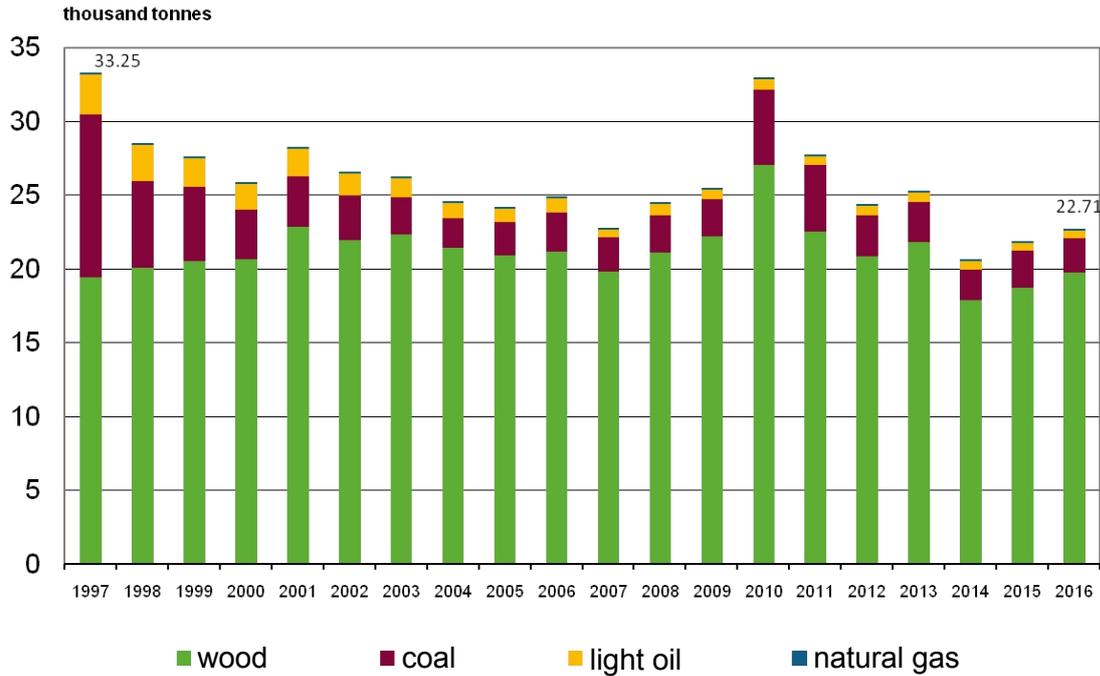


Figure 2: PM₁₀ emission from different sources including small combustion systems in Germany (Umweltbundesamt, 2019b)

According to the EU council directives 1999/30/EC and 96/62/EC, there are both long-term- and short-term limit values for particulate matter (both PM₁₀ and PM_{2.5}) in ambient air for the protection of human health. It mainly includes numerical limits and thresholds during two phases: first phase has been effective since 1 January 2005, with an annual mean value of 40 µg/m³, and a 24h average value of 50 µg/m³, which is not allowed to be exceeded more than 35 times per year. In the second phase, the annual limit value is restricted to 20 µg/m³, while the daily average is 50 µg/m³, but the number of days allowed exceedance, however, was reduced to seven times per year.

According to European Environment Agency (2019), about 13 - 42 % of the EU-28 urban population was exposed to PM₁₀ with concentrations in excess of the EU daily limit value from 2000 to 2017, indicating the limit values were exceeded frequently and widely in European regions. In Portugal, the daily PM₁₀ limit value has been exceeded since 2004 and, this exceedance would have decreased by 46 % when residential combustion was not considered according to the results from a modeling system (Borrego et al., 2010). High PM₁₀ levels in ambient air cause adverse effects on the environment. Even though this

problem is aware of, it is getting more and more serious due to extensive application of wood in this energy sector.

Health effect

Besides adverse effects on the environment, PM also poses health risks on human beings. Epidemiological studies show that ultrafine airborne particles are able to penetrate into the lung after inhalation, and effect on different organs and systems like the cardiovascular , respiratory and nervous system, causing heart attacks, lung diseases and asthma symptoms (Pope and Dockery, 2006; Kampa and Castanas, 2008; Huttunen et al., 2012).

Depending on the wood types and combustion conditions, PM formed during wood combustion has attached to different chemical components. The ones of great concern are condensable organic compounds including polycyclic aromatic hydrocarbons (PAHs), organic carbon (OC) and soot (normally defined as black carbon, BC). PAHs are a group of carcinogenic organic substances, among which benzo[a]pyrene (BaP) is recognized as very toxic. An annual average limit value of $1\text{ng}/\text{m}^3$ in ambient air is prescribed in the EU air quality standards (Directive 2004/107/EC, 2005; Directive 2008/50/EC, 2008). Exceedances of this value are however very frequent in central and eastern Europe, which lead to health risks on human beings and negative impact on local air quality (Guerreiro et al., 2018). Due to the high carbonaceous fraction of PM, health effects related to the exposure to PM from various combustion sources, including wood burning, is worldwide discussed (Naeher et al., 2007; Kocbach Bølling et al., 2009).

To summarize, PM pollution from wood burning for domestic heating has become a major problem in residential areas. Emission control of PM caused by residential wood burning is of great importance regarding human health and the improvement of air quality especially to meet EU requirements for the reduction of particulate matter.

1.3 Thesis structure

This study aims to carry out a source apportionment of ambient PM_{10} with the special focus on the contribution of wood burning in a specific residential area in Germany. The main structure of the thesis is depicted below (Figure 3). First a literature review is carried out with the focus on commonly used source apportionment techniques, which brings out the application principle and calculation method of the levoglucosan tracer method used later in the experimental part. This is followed by the specific motivations, objective and tasks in Chapter 3, as the experiments and results are discussed in Chapter 4, Chapter 5 and Chapter 6. Details about the experiments are listed later in Chapter 3.3.

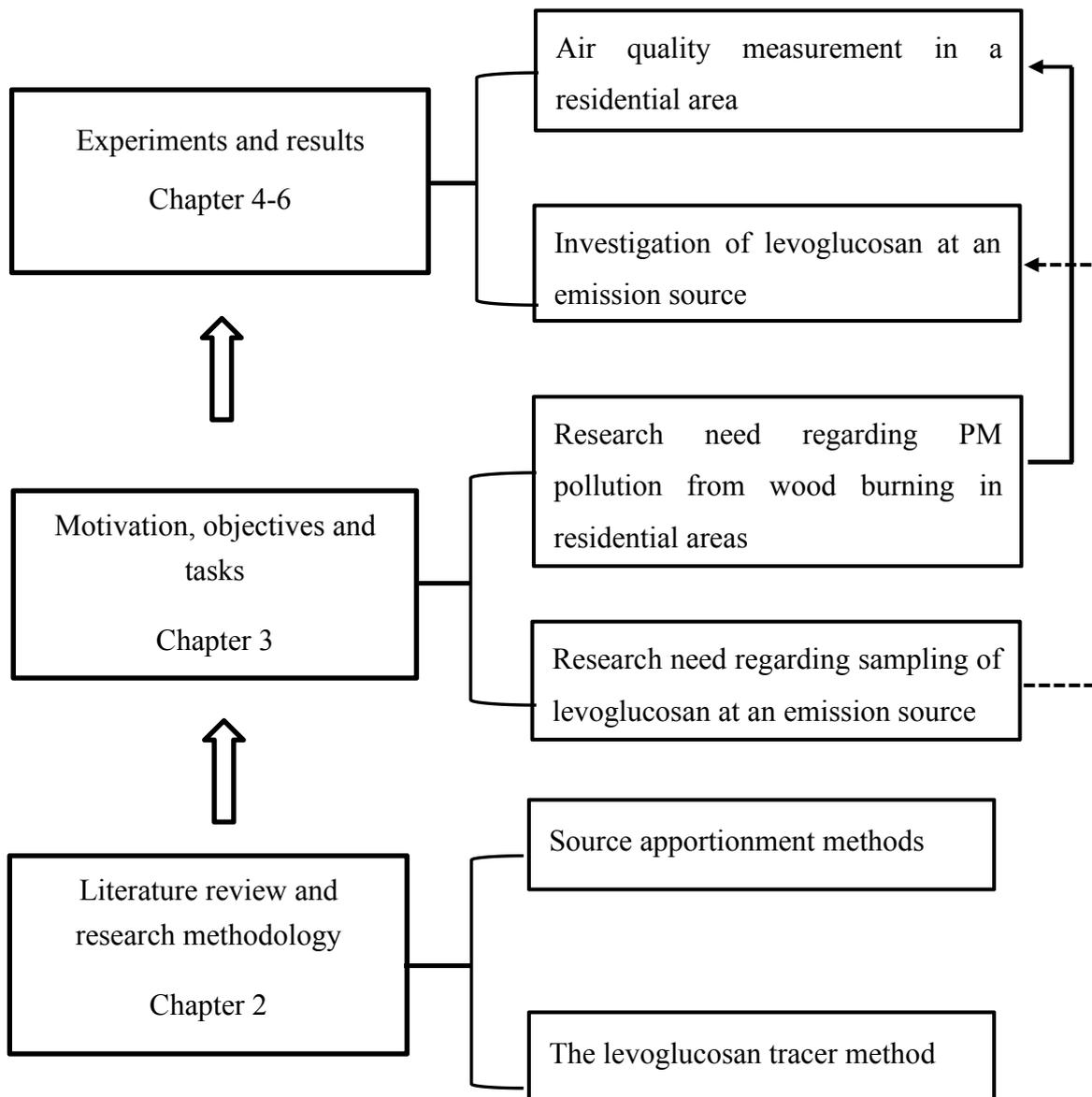


Figure 3: Main structure of the thesis

2. Literature review and research methodology: source apportionment of PM₁₀ in residential areas

Besides wood combustion, fine particulate matter has other potential anthropogenic emission sources like industry or traffic emissions. However, in residential areas in Germany, where wood burning for domestic heating is very common in winter periods and industry emissions can be excluded, wood combustion is presumed to be one of the predominant contributors to ambient PM₁₀. Due to the negative effect on the environment as well as on human beings, the emission level of PM₁₀ from wood combustion should be quantified for air quality control and to protect human health. This process is the so-called source apportionment, which is the technique used to evaluate the contribution share to a certain air pollutant from a specific source. Source apportionment of air pollutants is necessary and important because framing effective air quality strategies and implementation of rational and convincing policies are only possible after the correct assessment of impacts of each emission sources (Russell 1988).

2.1 Research topics relating particulate matter from residential wood combustion

Residential wood combustion (RWC) is an important issue in the research field of air quality control worldwide. One of the widely discussed topics is how to estimate the wood burning contribution to total ambient PM₁₀. In Europe, extensive and intensive research has been carried out in France, Germany, Austria, and from Nordic countries like Denmark, Norway and Sweden (Yttri et al., 2005; Hedberg et al., 2006; Glasius et al., 2006; Puxbaum et al., 2007; Krecl et al., 2007; Caseiro et al., 2009; Bari et al., 2010; Krecl et al., 2010; Fuller et al., 2014; Yttri et al., 2015).

Herich et al. (2014) concluded in his studies that PM from wood burning add often up to 50 % and more of the EU daily limit value for PM₁₀ in several alpine valleys during winter

periods. In Germany, PM from domestic wood stoves contributes significantly to total PM in the ambient air. The Bavarian Environment Agency (Bayerisches Landesamt für Umwelt, 2009) calculated that about 38 tons of PM₁₀ are emitted annually into ambient air from wood stoves, which account for up to 25 % of the total fine particle emissions in Augsburg. In Portugal, residential wood combustion contributes to 18 % of total PM₁₀ emissions (Borrego et al., 2010).

Situations are similar in Nordic countries. It is reported that residential wood combustion accounted for 25 % of the Finnish primary PM_{2.5} emissions in 2000, and this value increased to 40 % in 2010 (Karvosenoja et al., 2010; Saarnio et al., 2012; Kukkonen et al., 2018), while in Denmark more than 60 % of all Danish PM_{2.5} emissions are attributed to residential wood combustion in 2016 (Nielsen et al., 2016). A much higher share of 80 % is attained as wood combustion contribution in Oslo (Kauhaniemi et al., 2008). All these studies show that wood burning is one of the dominant emission sources of aerosols at many locations across Europe, in particular in the alpine region during winter periods. This pollution problem is also frequently investigated outside Europe like in North American, Australia, New Zealand and in South American (Reisen and Brown, 2006; Robinson et al., 2007; Reisen et al., 2011; Kotchenruther, 2016).

Other research topics relating PM from residential wood combustion include characterization of gaseous pollutants like VOC and CO, with the focus on PM-bound compounds like polycyclic aromatic hydrocarbons (PAHs), organic carbon (OC) or organic matter (OM) and soot (BC) (Johansson et al., 2003; Sippula et al., 2007; Boman et al., 2011; Pettersson et al., 2011).

PM-bound PAHs are carcinogenic organic compounds and relevant studies are considerable, in terms of individual PAH analysis, proportion of carcinogenetic PAHs or PAHs' diagnostic ratios, which are also applied to identify the origin of the PM source based on the idea that different emission sources have different PAHs profiles (Yunker et al., 2002; Zhang et al., 2005; Pies et al., 2008). In this study, PAHs and OC in ambient PM samples are investigated and discussed. Black carbon is discussed in detail in Chapter 2.4.

Besides these above mentioned ambient studies, emission research is also an important topic since the PM emission from wood burning experiments can be correlated to the wood burning PM found in ambient air. For example, Fine et al. (2001; 2002a; 2004a; 2004b) conducted a series of wood combustion experiments in fireplaces and wood stoves to establish the emission profiles of wood types grown in North America. Emission rates of organic compounds are calculated on the basis of OC. In Austria, Schmidl et al. (2008; 2011) aimed to create the specific profiles of PM₁₀ from wood smoke for woods and stoves used in Austria as representative of the mid-European Alpine region. These results are used by some other researchers for the calculation of the contribution of wood burning to PM or OC (Puxbaum et al., 2007; Saarikoski et al., 2008; Caseiro et al., 2009).

2.2 Methods for source apportionment

Different approaches have been brought out and developed to estimate the residential wood combustion contribution to ambient PM in these source apportionment studies (Szidat et al., 2006; Puxbaum et al., 2007; Caseiro et al., 2009; Favez et al., 2010; Lanz et al., 2010; Maenhaut et al., 2012). Based on the literature review, some of the commonly used methods are divided into two groups and briefly introduced in the following section. This classification is, however, only suggested for discussion in this study. Different classifications might be found in literature because some concepts are intercross.

2.2.1 Mathematical models

Mathematical models include both source-oriented and receptor-oriented models, which have been developed to predict the impact of specific emission source types on air quality (Schauer et al., 1996). With certain required input data, a model is able to apportion the measured PM at a receptor site to possible emission sources.

The fundamental principle of source-oriented models is to use emission inventory data, atmospheric diffusion and transport calculations to predict pollutant concentrations at specific air monitoring locations and to calculate the contribution of a specific source type (Bencala and Seinfeld, 1979; Schauer et al., 1996; Kleeman et al., 1997). These models are

based on various chemical constituents in a sufficiently large number of ambient particulate matter samples collected at the receptor site (Cooper and Watson, 1980; Watson, 1984). Assessment of model performance is based on the scientific principle, and the predicted results are usually compared with the measured pollutant concentrations at the sites, both spatial and temporal distribution (Bencala and Seinfeld, 1979). For example, MISKAM (Eichhorn and Kniffka, 2010) is a micro-scale flow and dispersion model based on CFD-code. This model requires the emission inventory (emission sources), meteorological conditions and dispersion calculation to determine wind field and to predict the spatial and temporal distribution of pollutant concentrations (Wang, 2007).

Commonly used receptor models are chemical mass balance (CMB), positive matrix factorization (PMF), principal component analysis (PCA), enrichment factors (EFs) and factor analysis (FA) (Sandradewi et al., 2008a; Favez et al., 2010; Harrison et al., 2013). CMB and PMF are widely used receptor-oriented models for source apportionment of ambient particulate matter and for prediction of pollutants dispersion in studies. CMB is based on source chemical components or more often on individual tracers of all relevant emission sources, which are used as input to reconstruct the measured concentrations of particle chemical components (Chow et al., 2007; Fuzzi et al., 2015). In comparison, PMF requires no prior knowledge of factor profiles and is often applied to data from aerosol mass spectrometers (AMS) (Aerodyne Research Inc.) for source apportionment of organic matter (Lee et al., 1999; Lanz et al., 2010; Pandolfi et al., 2011; Herich et al., 2014; Fuzzi et al., 2015; Miranda et al., 2018).

Based on the mass conservation law, receptor modeling technique relies on the assumptions that a fixed source profile exists, and chemical species of PM are chemically inert during transport from the sources to the receptor sites. However, in reality, source compositions are not constant, compounds are not chemical inert and there is a large number of important sources emitting PM without unique elemental composition. These kind of sources could not be identified in the ambient samples (Watson, 1984; Schauer et al., 1996). Moreover, sources which have similar chemical profiles could not be separated. These are the problems

and limitations of this technique. In recent years, a relative new technique called "Aethalometer model" is developed and has shown some advantage in revealing pollution load from biomass burning on ambient air quality (Harrison et al., 2012; Herich et al., 2014; Fuller et al., 2014). This model mainly involves the aethalometer measurement for black carbon which can absorb light. Nevertheless, these mathematical models are not the subject of this study and will not be discussed deeper. More details from fundamental principle, assumption, mathematical calculation and application examples could be found in literature (Cooper and Watson, 1980; Henry et al., 1984; Watson, 1984; Sandradewi et al., 2008b; Lanz et al., 2010; Favez et al., 2010; Belis et al., 2015; Fuzzi et al., 2015).

2.2.2 Tracer-based method

Another commonly used technique in source apportionment studies is called "tracer-based method". Tracers are chemical compounds having high source specificity. They could be directly linked to a specific combustion process, for example, biomass burning, and could be attained through chemically characterization of the aerosol (Rogge et al., 1993; Sheffield et al., 1994; Schauer et al., 1996; Fuzzi et al., 2015). The tracer-based method is actually a receptor-based method and could be applied to receptor modeling techniques like chemical mass balance (CMB). For example, Schauer et al. (1996) has developed a CMB receptor model based on the use of an organic tracer (Fine et al., 2004a). But the tracer method in this study is only referred to the method that calculates the contribution of a certain emission source by using the correlations between tracers and corresponding pollutants, both at an emission source and in the ambient air.

Categories of individual source tracer

Various compounds could be used as tracers to track emissions from wood burning, including both inorganic and organic tracers. Inorganic tracers are the chemical component of biomass, for example, water-soluble potassium (K^+ , also referred to non-sea-salt potassium (nss- K^+), black carbon (BC), sodium (Na^+), and others (Wolff et al., 1981; Sexton et al., 1985; Fourtziou et al., 2017). Organic tracers are chemical compounds formed in chemical reactions during incomplete combustion, for example, anhydrosugars (levoglucosan, mannosan and galactosan), PAHs, retene, methoxyphenols from lignin and

some other compounds like dehydroabietic acid, resin acids and syringols (Freeman and Cattell, 1990; Hawthorne et al., 1992; Simoneit et al., 1993; 1999; 2002; Zheng et al., 2002).

Different tracers have individual characteristics and application limitation. For example, vanillin and vanillic acid are specific for conifer wood, and methoxyphenols could be only detected from specific wood types. Besides, this kind of tracers is normally found to be minor compounds. For example, retene is emitted in a small amount and only from softwood. It was suggested that the use of retene should be of caution (Simoneit et al., 1999; 2002; Schmidl et al., 2008; Caseiro and Oliveira, 2012). Water-soluble K^+ is considered as more reliable and is the more often used wood burning tracers in recent source apportionment studies. However, K^+ has other potential emission sources and results must be corrected when K^+ is applied as tracer. Besides, potassium is a mineral element and K^+ is an ash component and could not be used as an indicator of incomplete combustion. Therefore, some suggested that K^+ might be more suitable as a tracer for ash (Schauer et al., 1999; 2001; Harrison et al., 2012). Radiocarbon ^{14}C could be also applied as a wood burning tracer and can lead to relative accurate result, but the high cost has limited its general application (Ramdahl et al., 1984; Szidat et al., 2006; 2007; Lanz et al., 2008). Therefore, these tracers are not widely used as general tracers for the source apportionment studies.

2.3 Levoglucosan as wood combustion tracer

However, another organic tracer called "levoglucosan" has been introduced and considered as an ideal wood burning tracer. It is very often used in atmospheric chemistry studies due to its advantages (Simoneit et al., 1999; Fine et al., 2001; 2002a; Schauer et al., 2001; Jordan et al., 2006; Schmidl et al., 2008).

Levoglucosan (1,6-anhydro- β -D-glucopyranose) ($C_6H_{10}O_5$) is an organic compound formed during the chemical pyrolysis reaction of cellulose and hemicellulose containing materials (biomass) at temperatures higher than 300 °C and is emitted as incomplete combustion product (Shafizadeh, 1968; 1984). The chemical structures of levoglucosan and its stereoisomeric anhydrosugars mannosan and galactosan are shown in Figure 4.

Levoglucosan is found to be emitted in a relative high amount and is the most abundant organic component of the identified compounds in smoke particles. Studies showed that levoglucosan makes up to 2 – 3 % of the organic carbon (OC) mass and accounts for an average of about 5 % of PM₁₀ from manually fired stoves, while methoxyphenols represent only 0.2 – 0.3 % of the OC mass on a carbon mass basis (Schmidl et al., 2011; George et al., 2016). Meanwhile, unlike K⁺ which has other potential emission sources, levoglucosan is almost exclusively emitted from cellulose and hemicellulose pyrolysis and it has not been found in other types of combustion processes except burning cellulose-containing substances so far (Shafizadeh, 1968; 1984; Locker, 1988; Simoneit et al., 1999; 2002; 2004). Besides, it is found to be very stable in ambient air. In a laboratory study by Fraser and Lakshmanan (2000), levoglucosan did not degrade over a period of 10 days when exposed to acid-catalyzed hydrolysis. Therefore, levoglucosan could be easily detected in ambient PM samples at receptor sites after transport through considerable distance (Locker, 1988; Simoneit, 2002). Compared to radiocarbon ¹⁴C method, levoglucosan is simple to measure and detected with relative low cost. All these mentioned properties make levoglucosan a valuable and universal tracer over others for tracking local biomass combustion emission (Lee et al., 2010).

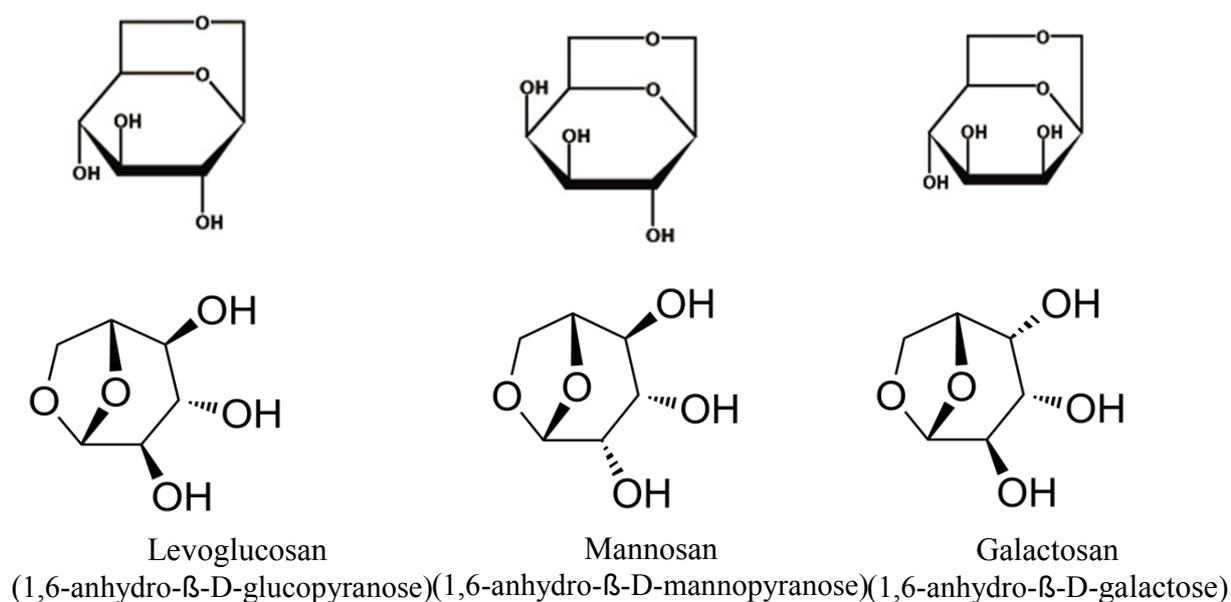


Figure 4: Chemical structures of the anhydrosugars

2.3.1 Controversial issues

However, in spite of the mentioned advantages, some researcher questioned the general applicability of levoglucosan as wood burning tracer, first due to the fact that emission levels and compositions of smoke particles and the emission levels of levoglucosan could be affected by several factors, and it is impossible to attain a constant emission ratio of levoglucosan under realistic burning conditions (McDonald et al., 2000; Jordan and Seen, 2005; Engling et al., 2006; Hedberg et al., 2006; Lee et al., 2010).

McDonald has pointed out that appliances and wood types have the largest effect on wood combustion emissions, and suggested that different profiles could be constructed for different wood types burning in different kind of stoves with different burning ways, which, however, could not be validated in reality (McDonald et al., 2000). In Portugal, Alves has investigated the chemical composition of fine particle emissions from Western Mediterranean wood types both in fireplaces and wood stoves and found that emission factors as well as smoke compositions vary with combustion technology and wood types (Alves et al., 2011). Another study shows that the fuel type has the dominant influence on variation of emission factor of levoglucosan, while operation conditions affect the emission factors only by a factor of 2 or 3 (Engling et al., 2006). This agrees with the findings from Jordan and See who investigated the variation of levoglucosan between different heater models and found very little variation of levoglucosan for a given heater compared to other particle-phase compounds, which indicates the potential use of levoglucosan as a general tracer for wood smoke (Jordan and Seen, 2005).

Another controversial issue of levoglucosan is about its atmospheric stability, which was questioned by Hennigan and Hoffmann, who suggested that levoglucosan might not be as inert as previously thought (Hennigan et al., 2010; Hoffmann et al., 2010). However, some other researchers argued that those findings are attained under certain measurement conditions with a high OH radical level, which is not likely to be relevant for most of the local source-tracking studies. As there is first of all no long-range transport, and secondly measurements are carried out in winter time when meteorological conditions do not favor

possible photochemical degradation of levoglucosan, this issue is considered to be of minor importance.

Therefore, despite of the above mentioned difficulties, questions and drawbacks, it is reasonable to conclude that levoglucosan is still an ideal tracer for wood burning. In fact, it is very often used as a mono-tracer or as one of the multiple tracers in source apportionment studies carried out in European cities like Paris, Berlin, London, Flanders, and alpine region sites (Puxbaum et al., 2007; Saarikoski et al., 2008; Caseiro et al., 2009; Favez et al., 2009; Favez et al., 2010; Maenhaut et al., 2012; Fuller et al., 2013; Fuller et al., 2014).

2.3.2 Application principle and calculation procedure

As mentioned before, so far there is no reference method available for source apportionment of ambient PM₁₀ regarding wood burning contribution. Various methods are applied and discussed in the literature, which is already reviewed above.

The general principle of the levoglucosan tracer method is that the fraction of the tracer in PM, i.e., the fraction of levoglucosan in PM (levoglucosan/PM) from an emission source should be known. This fraction is combined with the tracer fraction in ambient PM samples collected at a receptor site for the calculation (Herich et al., 2014). However, the experimental approaches to attain the fraction of levoglucosan in PM from an emission source differ from study to study in literature, and there are also various calculation procedures for the subsequent application of this value. Some definitions are inconsistent and unified in literature. To avoid misunderstanding, the definitions of two important terms mentioned in this study are clarified below before the calculation procedures applied in this study are discussed.

Definitions of emission ratio and emission factor

The fractions of tracers in PM are defined as emission ratios of these tracers here. Therefore, the emission ratio (ER) of levoglucosan is referred to the ratio of the mass of levoglucosan over PM mass with the unit % w/w (levoglucosan/PM in % w/w, see Equation 2.1). Only emission ratios of levoglucosan are involved in the following calculation procedure. The

emission factor is here only referred to the term used in literature but is not applied for the calculation in this study. The emission factor might have different units, depending on to which it is referred.

$$ER = (M_{Levo, emi} / M_{WBPM, emi}) \times 100 \% \quad \text{Equation 2.1}$$

$M_{Levo, emi}$ and $M_{WBPM, emi}$ are the masses of levoglucosan and wood burning PM measured directly at an emission source, respectively. Mass is in the unit of μg . ER is the emission ratio of levoglucosan and given as % w/w.

Calculation of wood burning PM and its contribution to ambient PM₁₀ using the levoglucosan tracer method

Firstly it should be pointed out that PM₁₀ is usually measured for air quality control in ambient studies. Therefore, all ambient PM in this study is referred to PM₁₀, which might be simplified as PM in the subscript. Total ambient PM₁₀ is referred to the total PM₁₀ collected on the filters at a receptor site. Wood burning PM in ambient air is here referred to the PM₁₀ portion generated from wood burning in the total PM₁₀ collected on the filters. Therefore, the wood burning contribution in a residential area is also referred to the sampling site.

The principle of using the levoglucosan tracer method is based on the fact that levoglucosan stems exclusively from biomass burning (Shafizadeh, 1968; 1984). In a pure residential area during winter periods, this can be referred to wood burning for residential heating. Since there is no other emission source for levoglucosan, its ratio to wood burning PM in the ambient air, which is determined through the sampling of ambient PM₁₀ on a filter, can be directly correlated to the ratio at the emission source, i.e., the ratio of levoglucosan to wood burning PM found on the filter should be the same as the ratio of levoglucosan to wood burning PM measured from the emission source, which can be described by Equation 2.2.

$$M_{Levo, amb} / M_{WBPM, amb} = M_{Levo, emi} / M_{WBPM, emi} \quad \text{Equation 2.2}$$

$M_{Levo, amb}$ and $M_{WBPM, amb}$ are the masses of levoglucosan and wood burning PM collected on the filter over a certain sampling period at the sampling site inside a residential area,

respectively. $M_{Levo, emi}$ and $M_{WBPM, emi}$ are already defined in Equation 2.1 regarding emission ratio ER.

By combining Equation 2.1 and 2.2, the following equation is attained.

$$M_{WBPM, amb} = M_{Levo, amb} \times 100 \% / ER \quad \text{Equation 2.3}$$

Therefore, the wood burning PM can be determined by measuring the mass of the levoglucosan on the filter and determining the emission ratio of levoglucosan at the emission sources. This equation fits for an area where only one type of wood is used. But the situation in reality is that different types of wood might be used and the consumption percentage of each wood type of the total wood consumption is also different. According to the study from Schmidl et al. (2008), this influencing factor can be taken into account in Equation 2.3 and shown as Equation 2.4.

$$M_{WBPM, amb} = M_{Levo, amb} \times 100 \% / \sum(P_i \times ER_i) \quad \text{Equation 2.4}$$

Where ER_i is the emission ratio of levoglucosan from wood types i (% w/w), P_i is the relative percentage (%) of wood type i in the total wood consumption structure in a residential area. A conversion factor (F_{loc}) is defined to cover these two parameters by Schmidl et al. (2008), which is shown in Equation 2.5.

$$F_{loc} = 100 \% / \sum(P_i \times ER_i) \quad \text{Equation 2.5}$$

This dimensionless conversion factor depends on not only the emission ratios of levoglucosan for different wood types used in a residential area but also the different consumption percentage of each wood type (wood consumption structure) (Schmidl et al., 2008). The conversion factor is called local conversion factor (F_{loc}) here since it has taken into account the local wood consumption situation.

By combining Equation 2.4 and Equation 2.5, a final Equation 2.6 is attained.

$$M_{WBPM, amb} = M_{Levo, amb} \times F_{loc} \quad \text{Equation 2.6}$$

Therefore, the wood burning PM in ambient can be calculated from Equation 2.6 if a local

conversion is known. Finally, wood burning contribution to total ambient PM₁₀ can be calculated by dividing wood burning PM by the total ambient PM₁₀, both referred to the mass collected on the filter.

To summarize, when calculating the wood burning contribution using levoglucosan as tracer, the principle is that levoglucosan/PM ratios from both the flue gas at an emission source and the ambient PM samples are required. The fractions of levoglucosan in PM at an emission source are to be measured and defined as emission ratios here. The emission ratio of levoglucosan for specific wood types and the knowledge about local wood consumption structure in an investigated area are required for the derivation of a conversion factor. This factor is combined with the tracer fraction in PM ambient samples collected at a receptor site in the investigated residential area.

2.3.3 State of art

Literature review: Studies where levoglucosan has been used as a tracer

From the above mentioned studies which aimed to characterize chemical profiles of fine particle and gaseous emissions from residential wood combustion, the emission ratios of levoglucosan from certain wood types could be determined (McDonald et al., 2000; Schauer and Cass, 2000; Fine et al., 2001; 2002a; 2002b; 2004a; Schauer et al., 2001). For example, it is found that emissions of levoglucosan from the burning of different wood species are in the range between 98 and 168 mg g⁻¹ on the base of organic carbon (Fine et al., 2001; 2002a). Schmidl et al. (2008) applied the weighted average levoglucosan content of wood smoke and calculated a conversion factor of 10.7 for wood smoke in Austria.

In Germany, there are some other studies trying to obtain a local conversion factor but using different derivation methods. A study carried out in Bayern region has derived a factor of 8 by using the correlation between potassium and levoglucosan (Bayerisches Landesamt für Umwelt, 2009), while Pfeffer et al. (2013) came out with a factor of 13 which is estimated through comparison of day and night ambient measurements with intensive wood burning near the sampling site. LUBW (2010) has derived the emission factor of levoglucosan based

on its correlation with potassium. However, most of these factors have not taken into account the wood consumption structure in the studied areas. There are also source apportionment studies investigating levoglucosan in ambient PM samples, while combustion experiments for obtaining emission ratios of levoglucose are missing.

These mentioned factors are widely used by other researchers (Fine et al., 2001; Zdráhal et al., 2002) especially the factor reported from Schmidl et al. (2008), which is adopted by many source apportionment studies in the Alpine regions. For example, Caseiro et al. (2009) applied the factors to calculate the relative contribution of wood smoke to PM in the Austrian region. In his another study, both this factor of 10.7 and a factor of 7.61 from Portugal for different cities within one project was used (Caseiro and Oliveira, 2012). Actually, considerations should be taken if a factor from other studies is simply applied since this factor might be not suitable for the own research cases. For example, Harrison et al. (2012) concluded in his study that the factor from Schmidl et al. (2008) might cause overestimation and could not be directly used in their case. Some researcher adjusted the available factor based on the situation in order to obtain reliable estimates of the wood burning impact on PM and OC concentrations. For example, after comparison of several derived factors from literature, Puxbaum et al. (2007) used one of the findings from Fine et al. (2002a) and converted it into a factor of 7.35 for the attribution of organic carbon in Europe background sites. In some studies, multiple individual tracers are applied and their correlation with each other are also investigated to overcome this drawback and seek for more accurate results (macro-tracer method) (Herich et al., 2014).

Some studies combined the application of levoglucosan with other methods and came to different conclusions (Elsasser et al., 2012; Harrison et al., 2012; Zhang et al., 2015; Fourtziou et al., 2017). Some found a good agreement between levoglucosan and the Aethalometer model (AE model) in terms of the estimated level of wood burning PM in London, while some concluded that the results from the levoglucosan method are more reliable to the AE model which is more subjected to other interference on the specific site (Caseiro et al., 2009; Caseiro and Oliveira, 2012; Elsasser et al., 2012; Harrison et al., 2012;

Fuller et al., 2014). This indicates that there is no general suitable method which fits everywhere and the application in each study site should be based on the local situation.

Nevertheless, the application of multiple-tracers methods and comparisons between the results within one study make more sense because of the fact that until now there is no reference method to validate the results from all the available methods. The calculation of wood burning contribution to PM₁₀ is an estimation based on certain assumptions, which all have individual drawbacks. Therefore, different techniques should be conducted and serve for a plausibility check to assure the quality (Herich et al., 2014). However, the inter direct comparison of the conclusions between studies might be difficult due to many reasons, for example, different laboratory analytical methods used for the quantification of the same tracer.

Focus and challenge: levoglucosan sampling at emission sources

Based on the literature review above, it could be seemed that the research focus of the levoglucosan tracer method are the emission ratios of levoglucosan from wood combustion with local-used appliances and wood types, whereas sampling of levoglucosan is the challenge of the wood combustion experiments.

Sampling of PM-bound levoglucosan is basically sampling of PM, either from ambient air or directly from emission sources. Sampling of ambient samples is relative simple under atmospheric conditions and a reference method is available as the European Standard (DIN EN 12341, 2014). In comparison, PM sampling direct from flue gas exhaust at a combustion source is much more complicated due to the very high temperature of hot flue gas. Reference methods for PM sampling at emission sources are different between different countries, for example, the hot stack sampling method is applied in Germany (VDI 2066 part 1), which covers the sampling of PM directly from hot flue gas in the chimney and the use of a gravimetric method for the determination of mass concentration. This reference method for PM sampling is, however, only able to collect existing solid particles in the hot flue gas. It is not suitable if the study aim is to capture volatile organic compounds in the

flue gas as most of them are not partitioning at existing particles and are still in gas and semi-volatile phases under high temperature. That is, hot stack sampling does not represent the realistic emissions in the atmosphere and it underestimates the particulate matter as condensable organic compounds might condensate when flue gas exhausts are diluted and cooled down by ambient air during dispersion.

Some studies have introduced dilution of hot flue gas, which enables the condensation of organic matter on PM so that it can be collected on the filter. The principle is that either partial flow or total flow of flue gas is diluted and cooled down to atmospheric temperature and pressure (near ambient conditions) with a dilution system, mainly a dilution tunnel, prior to sampling. In comparison to hot stack sampling method, the dilution method mimics the cooling, dilution and eventually the particle formation process from wood burning emissions and gives a better estimation of the realistic emission, the so-called 'real world' condition (Nussbaumer et al., 2008). Some studies have carried out the comparison of PM emissions between hot stack sampling and sampling with dilution and the results show that the mass concentrations from these two different sampling techniques differed by a factor of 12 (Johansson et al., 2004; Pettersson et al., 2011; Ozgen et al., 2014). Moreover, the dilution process enables the condensation of semi-volatile organic compounds on the particles which thus are collected in the particle phase. Therefore, it is commonly used in studies with the objectives of sampling particulate matter together with condensed organic compounds (Schauer et al., 1996; McDonald et al., 2000; Fine et al., 2001; 2002a; 2004a).

A "dilution tunnel" is a common dilution system, which can be applied for both partial flow dilution and full flow dilution. An example for a partial flow dilution system is a dilution stack sampler developed and introduced by Hildemann et al. (1989). One of the features of this dilution system is that the dilution air is activated carbon-filtered air to avoid possible interferences of the results. This system was developed and extended by several researchers in studies relating emission behavior of levoglucosan from different wood types (Schauer et al., 1996; Fine et al., 2001).

Full flow dilution is a dilution technique which uses ambient air as dilution air, either pre-cleaned or not, depending on the experiment objectives. The full flow dilution tunnel system together with the whole experiment set up are specified in the sampling reference method for particle emission measurement from residential combustion facilities in some countries. In the US, the US Environmental Protection Agency (US EPA) has brought out EPA method 5G (US Environmental Protection Agency, 2000), while in Norway it is Norwegian standard (NS 3058-2, 1994) and in Australia or New Zealand it is Australian/New Zealand standard (AS/NZS 4013:1999). The dilution tunnel system specified in Norway standard resembles the EPA method in many aspects. These two methods are widely applied in relevant studies (McDonald et al., 2000; Win et al. 2012; Ozgen et al., 2014). The main features of these dilution tunnel systems are that a hood is adjusted above the chimney, and the entire flue emission is drawn into the dilution tunnel where it is diluted with a larger volume of ambient air which is also drawn together through the hood. The dilution ratio can be regulated by controlling the volume flow of the dilution air. Definition and calculation of the dilution ratio are also prescribed in the reference methods.

Different dilution ratios from corresponding dilution systems found in literature are listed in Table 1 for comparison. It is observed that the dilution tunnel method is generally applied for the sampling of PM in combustion emission studies, most of which were interested in PM-bound PAHs and levoglucosan. The applied dilution tunnel systems are either self-developed or built according to standard methods, and the ranges of dilution ratios are different. Some varied between a relative wide width for example between 20 and 80 when partial flow dilutions are applied, and are, however, mainly lower than 10 in full flow dilution cases. Sampling temperature is in a similar range between 30 and 75 °C.

Therefore, the dilution sampling system is the trend but its construction and application are different depending on individual experimental objectives. For sampling of levoglucosan in the particle phase from combustion sources, the dilution technique instead of hot stack sampling should be applied to the hot flue gas like sampling of other organic compounds from the emission source. Thus, a dilution tunnel system is needed as part of the

experimental setup. By comparing these publications in detail, it is found that dilution ratios as well as achieved sampling temperatures are mentioned, but the potential impact of sampling techniques on levoglucosan was not investigated. No sampling temperature is specified in the reference method, but some research suggested that it should be kept in the range of 25 to 55 °C. These points lead to the detailed discussion about the motivation and objectives of this study in Chapter 3.

Table 1: Comparison of studies using the dilution method for PM sampling from residential wood combustion facilities

Dilution system	Dilution ratio and temperature after dilution (°C)	Studied Parameters (Organic compounds)	Source
Adopted from Hildemann et al. (1989)	25-80 fold excess air	Levoglucosan, PAHs OCEC and K ⁺	Schauer and Cass, 2000; Schauer et al., 2001
Modification from Hildemann et al. (1989)	20-40 for fireplace	PM, PAHs, OC/EC and K ⁺	McDonald et al., 2000
Dilution tunnel from Hildemann et al. (1989)	20-30 25-40	Levoglucosan, PAHs and OCEC	Fine et al., 2001; 2002a; 2002b; 2004a
AS/NZS 4013:1999		Levoglucosan	Jordan and Seen, 2005
Full flow dilution	3-7, 45-75 °C	PM and PAHs	Boman et al., 2005
Partial dilution with porous tube diluter	3-9, 50 °C	PM, VOC and OCEC	Sippula et al., 2007
Full flow dilution tunnel	1.5-4.3, 45-75 °C	VOCs, PAHs and total PM	Boman et al., 2011
NS 3058-2, 1994	25-240, < 30 °C	PM _{2.5}	Win et al., 2012
NS 3058-2, 1994	10, 30-35 °C	PM and PAHs(BaP)	Ozgen et al., 2014
	10-15, < 35 °C	PM and PAHs	Toscano et al., 2014
Self-built		Levoglucosan, PM ₁₀ , PM _{2.5} and OCEC	Calvo et al., 2014; 2015

2.4 Black carbon from wood combustion emission

Black carbon (BC), also called soot, is the light-absorbing fraction of carbonaceous particulate matter with a deep black appearance. As one of the key carbonaceous component in aerosol, black carbon has been intensively studied in the past decades in atmosphere research (Baumbach et al., 2016). The adverse effect of BC on human health is proved with evidence through short-term epidemiological studies, which show short-term health changes due to BC exposure (Janssen, 2012). Besides, BC is recognized as one of the dominant contributors to global warming as it absorbs solar radiation and scatters light (Ramanathan and Carmichael, 2008; Shindell, 2011; Bond et al., 2013). Studies of BC across Europe, in China and USA have shown that BC pollution is a serious problem worldwide (Chow et al., 2009; Reche et al., 2011; Lee et al., 2013; Ahmed et al., 2014).

In atmospheric research, the term BC is commonly mixed up with elemental carbon (EC) as their definitions are ambiguous and they are often used synonymously in literature. Recently, it has come to a general agreement that BC and EC are method-dependent definitions. That is, utilization of the terms BC or EC should be based on measurement techniques, whereas BC is an optical term used to refer light-absorbing carbonaceous aerosol measured by optical techniques, which might contain not only EC but also light-absorbing OC (Andreae and Gelencsér, 2006). EC is a thermal-chemical term used to denote the carbon fraction identified by thermal evolution methods like thermographic method and thermal optical reflectance (TOR), which have corresponding standard procedures (VDI 2465 part 2) or protocols (NIOSH), respectively (Chow et al., 2011; Bond et al., 2013; Petzold et al., 2013). Many efforts have been made to compare in-situ BC and thermal EC in order to find a conversion factor between these two methods in literature (Lavanchy et al., 1999).

Through the measurement of optical attenuation, the BC concentration could be estimated for ambient and source particles (Gundel, 1983). Some techniques have been well-developed for the in-situ measurement of real-time BC, for example, with a Multi-Angle Absorption Photometer (MAAP) and an aethalometer. Until now there is no standard referring measurement technique for BC. The aethalometer is one of the most widely and extensively

used device to measure temporal variations of BC concentrations. This study includes also the application of an aethalometer for BC measurement in ambient study, and the working principle is shortly described below. Information about other devices is not the subject of this study.

The application of the aethalometer involves first PM sampling on a filter base. Light beams produced from a light source pass the filters and the decrease of light transmission due to light-absorbing BC (also called attenuation of light) is measured and converted into BC mass concentration in ng/m^3 based on the sample volume and some manufacture defaults. The aethalometer model applied in this study is AE33 (Magee Scientific 2014, Berkley, CA, USA), the newest model when the measurement was carried out. The AE33 is able to continuously measure BC mass concentration in-situ with 7 channels. The direct output of BC concentration is based on the measurement at channel 6 with a wavelength of 880 nm, at which it is assumed that the absorption is caused only by BC, while absorption from other material is negligible. Another prominent feature of the Aethalometer AE33 is that it is able to perform source-apportionment of BC and deliver a direct output of biomass burning BC (BB%) based on the mathematical model from Sandradewi et al. (2008). Both concentration and biomass burning BC are reported and discussed in this study. Further description about the principle of AE will be mentioned in Chapter 5 for introduction of measurement techniques for ambient measurement.

Major emission sources of BC are fossil fuel burnings from traffic section and uncompleted biomass burning in residential heating. Research of ambient BC is found in plenty in literature. The focus of these studies cover not only the ambient concentration of BC, but its correlation with other pollutants like CO and PM, which could be used for identification of BC from biomass burning or for estimation of BC emission with available annual CO emission (Chow et al., 2011; Meyer, 2012). Meanwhile, BC concentration in ambient air is affected by meteorological variables, for example, wind speed and dynamic layers. Therefore, interpretation of measurement results should be also combined with meteorological data.

3. Motivation, objectives and tasks: wood smoke in ambient air

Based on the literature review in Chapter 2, PM pollution from residential wood burning is a common issue in European countries and considerable studies are carried out by researchers, trying to trace and quantify the contribution from wood burning to ambient PM₁₀ using different apportionment techniques.

3.1 Research need and motivation

3.1.1 Research need in the studied residential area

A previous study (Bari et al., 2009) has investigated the air pollution problem in a residential area in Dettenhausen, which is a small town located in the south of Stuttgart, Germany. Wood burning for room heating during winter periods is very intensive there. Therefore, this area suffers also under PM pollution from residential wood burning heavily in winter times especially under inversion weather conditions.

Characterization of PM was carried out with the focus on particle-bound PAHs, where PAH ratios and profiles are used to identify PM from wood combustion (Bari et al., 2010). Levoglucosan from both ambient PM samples and emission samples was also investigated together with methoxyphenols, dehydroabietic acid and retene as tracers for source identification (Bari et al., 2009). Results from these previous studies show clearly that local air quality in the village was strongly affected by residential wood burning. Residents complain very often about the bad air quality and strong unpleasant smell from wood smoke. Therefore, a further and deeper study of wood smoke pollution in this area is necessary, with the focus on the quantification of the wood burning contribution to ambient PM.

3.1.2 Research need of levoglucosan as tracer for source apportionment of ambient PM₁₀

For the source apportionment of ambient PM₁₀, the levoglucosan tracer method can be used based on the discussions in Chapter 2.3. The application of this method requires firstly the emission ratios of levoglucosan referred to PM at an emission source, which can be realized by sampling of levoglucosan in PM with a dilution technique from wood combustion experiments. According to the calculation method published by Schmidl et al. (2008), a local conversion factor regarding levoglucosan from different locally used wood types needs to be derived based on the local wood consumption structure. This factor can be applied directly for the calculation of wood burning contribution to ambient PM₁₀ in this area.

3.1.3 Sampling conditions for levoglucosan at an emission source

During the compose of this thesis, a draft standard regarding levoglucosan measurement in ambient air is published (VDI 2444, draft), which specifies the sampling equipment, sampling procedure and chemical analysis method for levoglucosan. However, so far there is no reference method which specifies sampling conditions for levoglucosan at an emission source. To the author's knowledge, there is no systematic study about influence of sampling parameters on the detected emission levels of levoglucosan. Very few studies have covered the discussion about emission dependence of levoglucosan. One example is the research from Jordan and Seen (2005) who investigated the variation of levoglucosan emissions between different airflow conditions for a given wood heater and found the variation relatively little. A similar study from Boman et al. (2005) investigated the influence of dilution sampling conditions on emission characteristics of particulate matter and PAH, however, levoglucosan was not investigated.

Therefore, parameters that actually play a role on the amount of levoglucosan condensated on PM is unknown, i.e., the effect of dilution ratio or sampling temperature on the detected amount of levoglucosan on the filter. For example, which temperature could be achieved by using a dilution tunnel with a certain dimension? Is the retention time long enough for the condensation of levoglucosan? These questions are of research interest. By answering these

questions, it is expected to suggest a simple and suitable sampling procedure for levoglucosan using the dilution method at emission sources.

3.1.4 Levoglucosan emission from different combustion phases

The emission behaviors of levoglucosan during one combustion cycle in wood stoves are not fully understood. Schmidl et al. (2008) and Calvo et al. (2014) have detected different amounts of levoglucosan from samples collected from different combustion phases in their experiments. But correlations between the emission level and parameters during the different phases are not discussed. There are still some open questions, for example, how is the evolution of levoglucosan during different combustion phases? Can levoglucosan emission be correlated with other pollutant emissions like VOC, CO and smell of wood smoke? Answering these questions is one of the motivations of this study.

3.2 Research objectives and tasks

Based on the motivations, the main research objective of this study is to quantify wood burning contribution to ambient PM₁₀ with regard to the air quality situation in Dettenhausen using the levoglucosan tracer method, which requires the investigation of levoglucosan at an emission source and the measurement of levoglucosan in ambient air.

Therefore, the first task is the measurements of various ambient air pollutants during winter periods in this residential area. Meteorological parameters should also be measured in order to get a better understanding of the pollutant dispersion. A short term study of indoor air quality inside a resident's house in the investigated area is performed in order to investigate whether the indoor air quality is polluted by wood burning products or not.

For the sampling of PM-bound levoglucosan from wood combustion experiment, a full flow dilution tunnel is designed and constructed based on some standardized methods. With two different sampling methods, the influences of different operation conditions and sampling parameters on levoglucosan emission are investigated: emission ratios of levoglucosan can be calculated and subsequently used for the derivation of a local conversion factor for the source apportionment of ambient PM₁₀.

The difficulty in the calculation of a local conversion factor is that in most of the cases, the wood consumption structure in a certain region is unknown and exact information is impossible to attain. It is suggested that scenarios with different cases of local wood types could be assumed for a rough estimation. Therefore, in this study, different shares of local wood types are proposed with the two commonly used wood types in the investigated area.

The specific content of each task is defined under each experiment component and is listed as follows:

- (1) To measure the ambient air pollutants in terms of PM₁₀, gaseous pollutants (NO_x and CO), black carbon and particle-bound PAHs and levoglucosan in Dettenhausen
- (2) To assess indoor air pollution from measuring wood combustion products indoor
- (3) To design and construct a dilution tunnel according to the EPA method 5G (US Environmental Protection Agency, 2000) and Norwegian standard (NS 3058-2, 1994)
- (4) To study the sampling process of levoglucosan from wood combustion experiments with this self-constructed dilution tunnel and to suggest suitable sampling conditions
- (5) To study the emission behavior of levoglucosan during different combustion phases
- (6) To calculate the emission ratios of levoglucosan from locally used wood types
- (7) To derive a local conversion factor based on attained emission ratios and assumed scenarios of wood consumption structure
- (8) To calculate the contribution from wood burning contribution to ambient PM₁₀ using the conversion factors in the studied area.

3.3 Experimental approach

According to the mentioned research objectives, the framework of this study should cover an ambient air study and emission research. Two experimental components corresponding to these two main tasks are designed to correlate with each other in terms of levoglucosan, PM₁₀ and black carbon as shown in Figure 5.

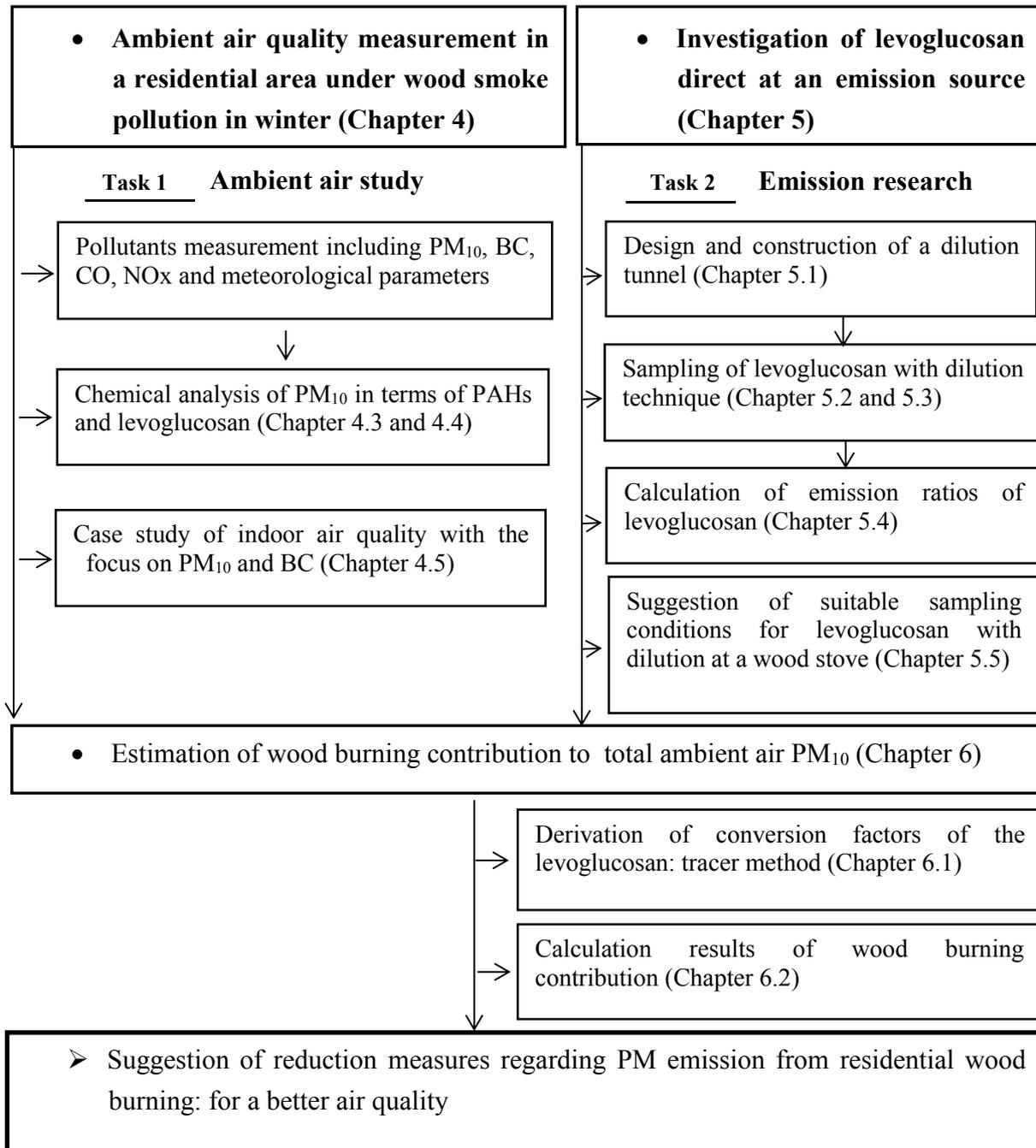


Figure 5: Schematic diagram of the experiment approach for the implementation of the objectives

4. Winter measurement of ambient air pollutants in a residential area

Based on the research need and motivation stated in Chapter 3, winter measurements of ambient air pollutants were carried out in the selected residential area in Dettenhausen in Germany, where a pollution problem from residential wood burning is recognized by using PAHs as source profiles for several source contributions (Bari et al., 2009). The aim of the ambient study in this residential area is to monitor and subsequently evaluate air quality under PM pollution from residential wood burning during winter heating periods, with the focus on PM₁₀, wood burning tracer levoglucosan and black carbon (BC).

4.1 Measurement strategy

4.1.1 Measurement site

Dettenhausen is a small town in the southern part of Germany and covers 11.02 km² with a population of 5495 (Gemeinde Dettenhausen, Stand April 2018). In this area, relative cold winters are occurring which last from November to next March with an average temperature normally below zero degrees in January and February. Inversion weather happens frequently in winters. The local topography is characterized by valleys, which can trap emissions and hinder the transport of PM and other air pollutants. Housing construction in this area is relative uniform and the neighbourhood closed to the measurement site is mainly characterized by two or three floor houses with chimneys. As to outdoor environment, most of the surrounding area is covered by greenery and there are no factories or industries nearby. Big shopping centers or markets are in a certain distance from the neighborhood.

4.1.2 Measurement program

There were two measurement campaigns for air pollutants covering winter heating periods from 2013/2014 and 2014/2015. The measured compounds included discontinuous measurement of particulate matter (PM₁₀), continuous measurement of black carbon (BC),

NO_x (NO₂ and NO), CO and meteorological parameters such as wind direction, wind velocity and temperature. Meteorological conditions are related to air pollutant dispersion in the form of favoring or hindering the transport of pollutants especially particles.

During the measurement campaigns, the IFK measurement van equipped with various measurement instruments was parked on a parking spot by a two-way street named 'Schoenbuchstrasse' (See Figure 6). Houses are near the street, and the chimney emissions are affecting the measurement spot. Besides the measurement station of the van, another measurement site was chosen for PM₁₀ sampling in order to investigate the spatial variation for winter 2013/2014. This site is on the roof of a house garage and is about 100 meter away from the measurement van. During winter 2014/2015, a short-term study of indoor air quality in a residential house was conducted for a few days to investigate possible pollution affect from wood burning products (Table 2).



Figure 6: Measurement van in neighbourhood (an inversion event in February 2015)

Table 2: Summary of two measurement campaigns

Campaign season	Period	Measurement compounds	General weather condition	Additional measurement
Winter 2013/2014	Dec 2013- Mar 2014	PM ₁₀ , NO _x , CO, meteorological parameters	Relative warm winter with some inversion periods	One more site for PM ₁₀ sampling
Winter 2014/2015	Nov 2014- Mar 2015	PM ₁₀ , NO _x , CO, meteorological parameters and BC	Relative warm winter with some inversion periods	Short-term study of indoor air quality

4.2 Measurement techniques

4.2.1 Equipment and materials

A gravimetric method was used for determination of PM₁₀ concentration according to the standard gravimetric measurement method (DIN EN 12341, 2014). Briefly, particulate matter was sampled using a low volume sampler (KleinfILTERGERÄT LVS 3.1, Comde- Derenda GmbH, Germany) with a sampling head for particles with a dynamic diameter not larger than 10 micrometer (PM₁₀) on a quartz fiber filter (47mm, Munktell & Filterak, Germany). Sampling durations were, however, adjusted to between 24 and 96 hours to ensure to collect enough mass for analysis, which depended on the weather conditions. Procedures for filter preparations and handling of loaded filters were carried out as specified protocols in the above standard. Loaded filters were only accepted as valid when the total mass of PM on the filter was not less than 0.6 mg. Through the measurement campaigns in two winters, a certain amount of loaded filters were attained. The specific objective relating these PM samples was, firstly, to determine ambient particulate matter (PM₁₀) concentration and subsequently to chemically analyze PM compositions in terms of PAHs, levoglucosan and organic carbon and elemental carbon. The filter sampling for a certain time period and subsequent chemical analysis in the lab is known as discontinuous manual measurement. Other pollutants (black carbon, NO_x and CO) and meteorological parameters were

continuously monitored with different time resolutions and the attained data were ready for later processing and evaluation.

Table 3: Measurands and corresponding measurement devices

Measured Parameter	Equipment	Mode	Range	Data recording and documentation
PM ₁₀	Low volume sampler (Derenda)	discontinuously		weighed and analyzed in the lab
PM ₁₀	Grimm Portable Aerosol Spectrometer and Dust Monitor Model 1.108*	continuously	0.1 -100.000 µg/m ³	automatically saved in the memory for later processing and evaluation
BC	The Aethalometer AE 33			
NO _x	NO/NO _x analyzer (Horiba APNA-350E)		0-1000 ppb	
CO	CO analyzer (Horiba APMA-360)		0-20 ppm	
temperature	Ultrasonic anemometer (Metek USA-1) and Anemometer and wind vane		0.5h most frequent	
wind speed				
wind direction				
*used only in indoor air measurements (see Chapter 4.5)				

It should be noticed that the Aethalometer for black carbon measurement was only available for the campaign in winter 2014/2015. As already introduced in Chapter 2.4, the Aethalometer® is the most widely used instrument for ambient black carbon measurement based on light absorption of aerosol at different wavelengths and conversion of attenuation through the filter (Allen, 1999; Kirchstetter et al., 2008). Aerosols are collected from an air stream passing through the filter and the optical attenuation (ANT) of a light beam through this filter is measured and converted to real-time mass concentration of black carbon (Magee Scientific 2014, Berkley, CA, USA). Model AE33 was the newest available model when the campaign was carried out. It incorporates a DualSpot method which not only compensates the ‘aerosol loading effect’ but also carries out the source apportionment of BC emissions based on the mathematical model from Sandradewi et al. (2008c). BC concentrations in

ng/m³ and biomass burning BC in the form of BB% are two major direct outputs from AE33. More details about the principle and development could be found in manual and other studies (Weingartner et al., 2003; Sandradewi et al., 2008c; Herich et al., 2014).

4.2.2 Chemical analysis method for PM samples

After gravimetric determination of PM₁₀ concentration, the collected samples were prepared for chemical analysis in the laboratory for further investigation of the particle-bound compositions - PAHs and wood burning tracer levoglucosan. Some selected samples were also analyzed for organic carbon (OC) and elemental carbon (EC).

Polycyclic aromatic hydrocarbons (PAHs)

PAHs especially BaP were of research interest in ambient PM samples due to their carcinogenicity and their negative effect on human health as explained in Chapter 1 and 2. Studies on aerosol-bound PAHs can be found in plenty of papers (Kawanaka et al., 2008; Barrado et al., 2012; Alves et al., 2017; Pongpiachan et al., 2017 and Pratt et al., 2018).

In this study, the chemical analysis of the PM samples was carried out using the internal standard method with GC/MS for 16 PAHs, which were issued by the United States Environmental Protection Agency (US EPA) on the priority pollutant list as they are found frequently in environmental samples (Keith, 2015). Abbreviations of the compounds, gas/particle phase distribution, and weights of internal standards molecular can be found in the literature. Specific experimental procedure related to extraction, concentration and injection on the GC/MS was similar to that discussed in the work from Bari et al. (2009). To describe briefly, it included adding internal standards (16 deuterated PAHs in toluene, 1 ng/ml) to filters before extraction with toluene as solvent and ultra-sonic agitation. And then the combined extracts were filtered and concentrated to 100 µl under a mild nitrogen stream. Finally, 1 µl of extract was injected into the GC/MS and the quantification was based on the retention time and spectra of analysts compared with the authentic standards. The analysis of PAHs was carried out in the laboratory in the Institute for Sanitary Engineering, Water Quality and Solid Waste Management (ISWA).

Levoglucosan

GC/MS is also commonly used for levoglucosan detection. However, the shortcoming of this method is that it requires a derivatization process of levoglucosan, which is very time and resource consuming.

Different from this, ion chromatography (IC) coupled with a pulsed amperometric detector (PAD) method (IC-PAD method) requires no derivatization step and the calibration covers a wide range. Filters attained in this study were analyzed for levoglucosan with this method in the laboratory in State Office for Nature, Environment and Consumer Protection in Nordrhein-Westfalen (LANUV). Briefly, sample preparation included addition of 40 ml ultrapure water and 60 minutes shake for the following ultrasonic extraction. Samples were filtrated prior to injection. Detailed information about this method is very similar to that described in Application Note 54 from Metrohm (2016).

Organic carbon (OC) and elemental carbon (EC) analysis

Some filters selected from the inversion period in winter 2014/2015 were also analyzed for OC/EC in the laboratory in LANUV with the application of a SUNSET equipment OC-EC Aerosol Analyzer based on the NIOSH method (Sunset Laboratory Inc., 2019). The above mentioned methods are listed in Table 4. Due to the limited capacity of the equipment, only 10 filters were analyzed, and the results are discussed together with levoglucosan in the later sections.

Table 4: Chemical analysis methods for different compounds from PM samples

PM-bound compounds	Chemical analysis method	Laboratroy
Polycyclic aromatic hydrocarbons (PAHs)	internal standard method with GC/MS (EPA)	at ISWA
Levoglucosan	ion chromatography coupled with a pulsed amperometric detector (IC-PAD method)	at LANUV
Organic carbon and elemental carbon (OC/EC)	Sunset OC-EC Aerosol Analyzer based on NIOSH method	

4.3 Results of ambient air measurements

In this section, the results based on the measurement campaigns for ambient air pollutants are firstly discussed with the focus on PM₁₀, particle-bound PAHs and Black Carbon. Results of levoglucosan content from PM samples and of indoor measurement are presented separately in Chapter 4.4 and in Chapter 4.5, respectively.

4.3.1 PM₁₀ concentration under different meteorological conditions

PM₁₀ is of most interest in this study as particles are the major pollutant from wood burning. Furthermore, it is the substrate for subsequent chemical analysis of PAHs and the wood burning tracer levoglucosan. The PM concentration in ambient air is strongly correlated to both emission sources and local weather conditions. For example, air turbulence might prevent or favorate pollutants dispersion. The ambient temperature is the main factor influencing the heating behavior of residents and is also of great importance. Therefore, the PM₁₀ level was evaluated together with local meteorological conditions in terms of the above mentioned variables.



Concentration: 27.8 $\mu\text{g}/\text{m}^3$



Concentration: 45.5 $\mu\text{g}/\text{m}^3$

Figure 7: Collected PM₁₀ filters (left: from December 2013, right: from March 2014)

Two PM samples with different concentrations from the same sampling site are shown in Figure 7. It can be seen that the filters appear in different colours and have different concentrations, the darker black colour is correlated with a relative high PM₁₀ concentration in this case.

4.3.1.1 Comparison of PM₁₀ and PM-bound PAHs from two measurement sites in winter 2013/2014

As mentioned before, one more low volume sampler was set up at a different site for PM₁₀ sampling during the measurement campaign in winter 2013/2014. The measurement site where the measurement van stand was defined as "standard site" and the other was named as "roof of garage". In total 35 filters have been collected at each site from December 2013 to March 2014. The start and end of the sampling for each pair of filters were almost simultaneously with a time difference of no more than 5 minutes. The calculated PM₁₀ concentrations and PM-bound PAHs are compared in Figures 8 and 9 below.

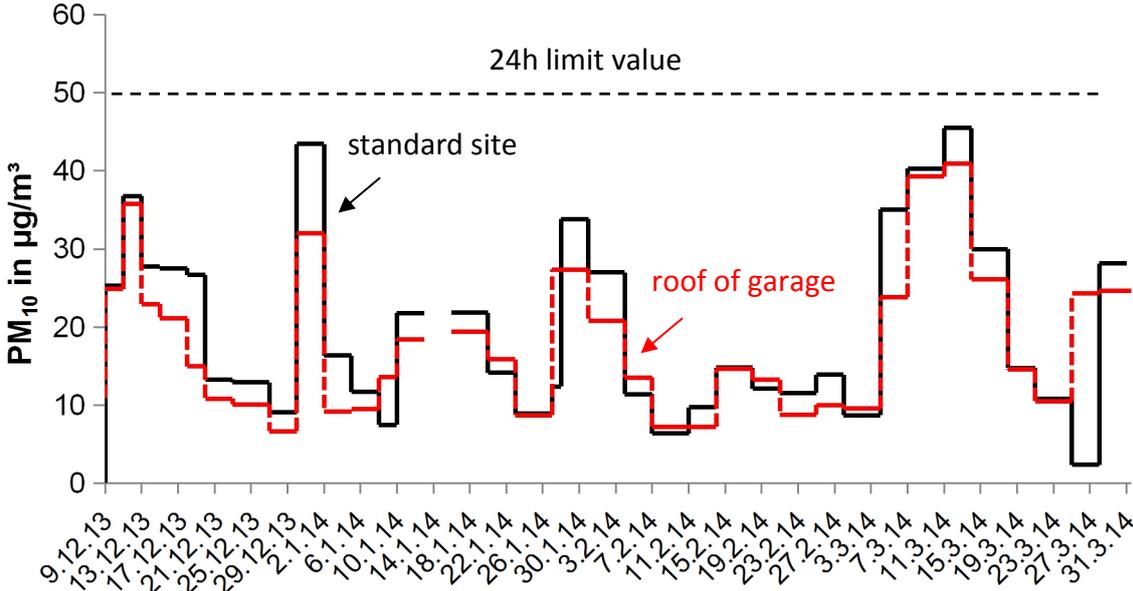


Figure 8: Daily averages of PM₁₀ concentrations at two measurement sites from December 2013 to March 2014

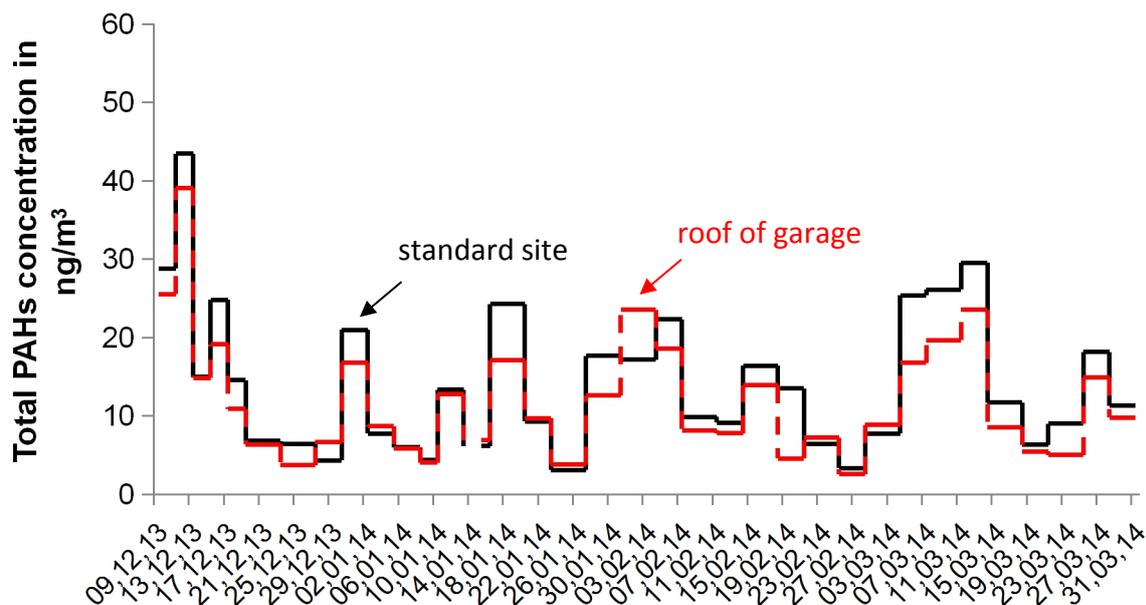


Figure 9: Daily averages of total PAH concentrations at two measurements sites from December 2013 to March 2014

First, all daily average PM_{10} concentrations are significantly lower than the 24h limit value of $50 \mu\text{g}/\text{m}^3$, with a slightly higher average concentration at the standard site in general. The averages for the standard site and roof of garage are $20.2 \mu\text{g}/\text{m}^3$ and $18.8 \mu\text{g}/\text{m}^3$ with standard deviations of 12.3 and 9.9, respectively. The difference is relative low and not substantial when taking into account the standard deviations. Figure 9 shows that total PAHs concentrations from both sites appear also with minor differences. The fluctuation profile of PAHs is also similar as that of PM_{10} .

With regard to PM and PM-bound PAHs, it is concluded that the concentrations at these two measurement sites are comparable, indicating both are affected by the same local PM emission sources. This very good agreement validated the experiment procedure. Therefore, only the results from the standard site are discussed in the following section if not otherwise mentioned. On the other side, eventhough all daily average PM_{10} is within the 24h limit value, there was a visible air pollution problem in this area (wood smoke and unpleasant odor). Results from PM-bound PAHs also reveal that the air quality was correlated to toxic substances.

4.3.1.2 PM₁₀ in winter periods from 2013-2015 with inversion periods

The temporal course of PM₁₀ concentration determined from samples attained from winter 2013/2014 and winter 2014/2015 is presented in Figure 10 below. It can be seen that PM₁₀ concentration from both campaigns fluctuate through the sampling period, and the differences between the minimal and maximal concentrations are relatively high. Daily average values in winter 2013/2014 are all below the EU 24h limit value of 50 µg/m³ as already shown before, with an average and maximal concentration of 20.2 µg/m³ and 45.5 µg/m³, respectively. In winter 2014/2015, there was one sample exceeding 50 µg/m³, which was collected during the inversion period 2 (See Figure 10). The average concentration is namely the same as that in the former winter with 20.1 µg/m³. In total a few daily average values are above the annual mean value of 40 µg/m³. The winter period is supposed to have the higher PM concentration than other seasons, when there is no residential wood burning, i.e., no PM contribution from this emission source. Therefore, it is logical to conclude that the annual mean value of 40 µg/m³ is not exceeded for a whole year in this residential area.

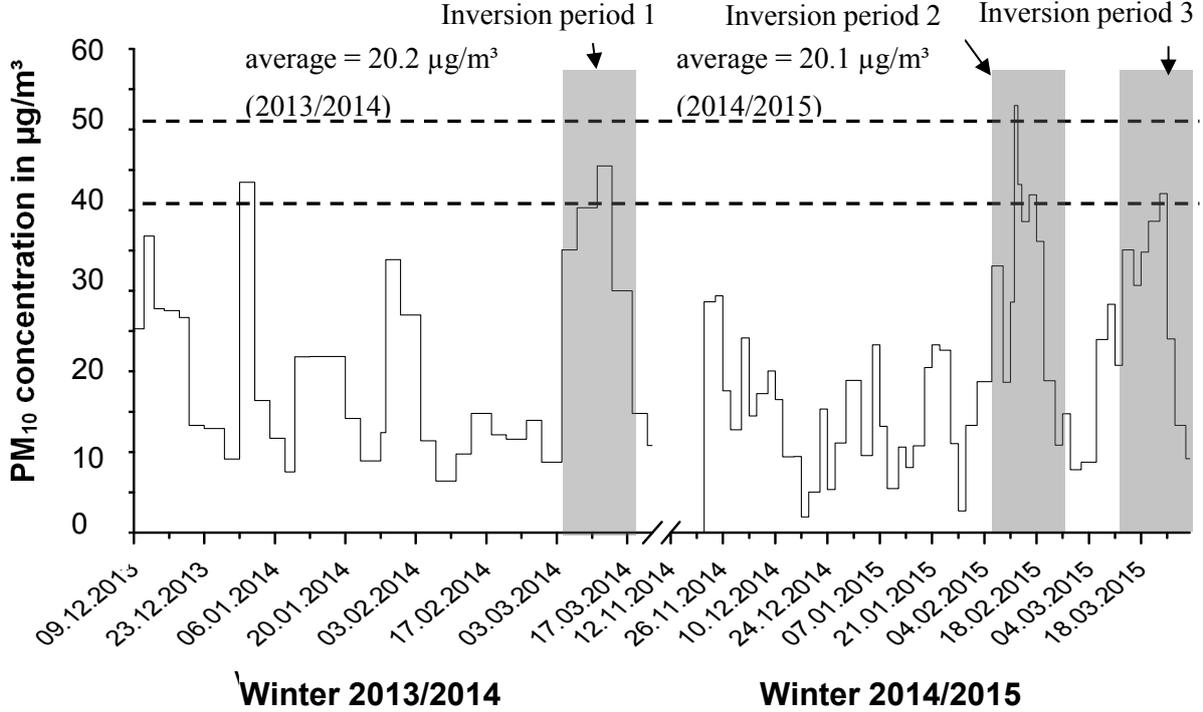


Figure 10: Daily averages of PM₁₀ concentrations in two winters

A few peaks which show relative high PM concentrations and lasted for a few days are observed in Figure 10, one was in March 2014, the other two in February and March 2015, respectively. These peaks represent concentrations under inversion periods, which imply the influences from the emission sources and as the dispersion situation as well. If the emission sources were constant in the area, concentrations of air pollutants are mainly subjected to weather conditions. However, this is not true as during inversion, it is colder and more combustion activities are occurring. Figure 11 shows the village under an inversion event in a winter morning.

Meteorological parameters in terms of temperature, wind (wind speed and wind direction) and air turbulence are important for pollutant accumulation and dispersion. With refer to the temperature trend measured in March 2014 as shown in Figure 12, the temperature shows a typical day-night pattern for the highlighted periods. During the day, the temperature ascends significantly after sunrise and descends also sharply at night after sunset. This temperature difference between day and night affected on the one hand the residents' heating behavior, which was, during the day it was relative warm (could be as high as 20 °C) and most of the people already turned off the central heating (supplied normally by oil or gas). The temperature was relative low (close to 0 °C) during the night, people preferred to heat the room with wood burning. On the other hand, this temperature pattern resulted in a surface inversion during the night. This inversion was dissolved very slowly in the morning because the solar radiation was still very weak in March, resulting in slow warming up of the ground. Therefore, it was very common to see inversion layers during the morning hours in winter months.

Inversion layers are significant to meteorology because they prevent atmospheric flow and cause the air become stable. This phenomenon can result in various types of weather patterns. More importantly, areas with heavy pollution are prone to unhealthy air and smog can happen because inversions trap the pollutants within the ground level instead of circulating them away.



Figure 11: Winter morning with temperature inversion inside the investigated residential area (Photo by G. Baumbach)

The inversion in March 2014 could be also observed from the measured wind speed as it is another parameter representing the circulation of air mass. It is obvious that the measured wind speed in this month shows a similar pattern to the temperature pattern in inversion periods (Figure 13). During the day, the inversion is slowly dissolved with increased temperature, and there is a mixing of air mass und consequently pressure difference presented. Therefore, the wind is detected during the day with the maximal wind speed. At night, when temperatures decrease and inversion is formed again, the air layer is stable and there is nearly no wind (wind speed close to zero) and pollutants cannot be dispersed. The wind speed during the inversion periods is obviously lower compared to those days without inversion. PM_{10} in this corresponding month in Figure 14 appears with higher concentrations during the inversion periods as expected.

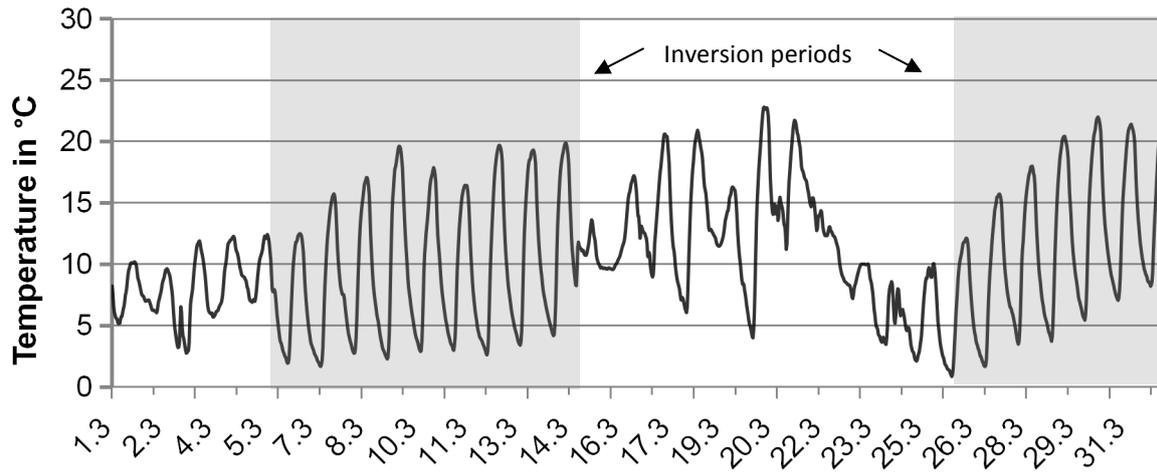


Figure 12: Temperature course in March 2014

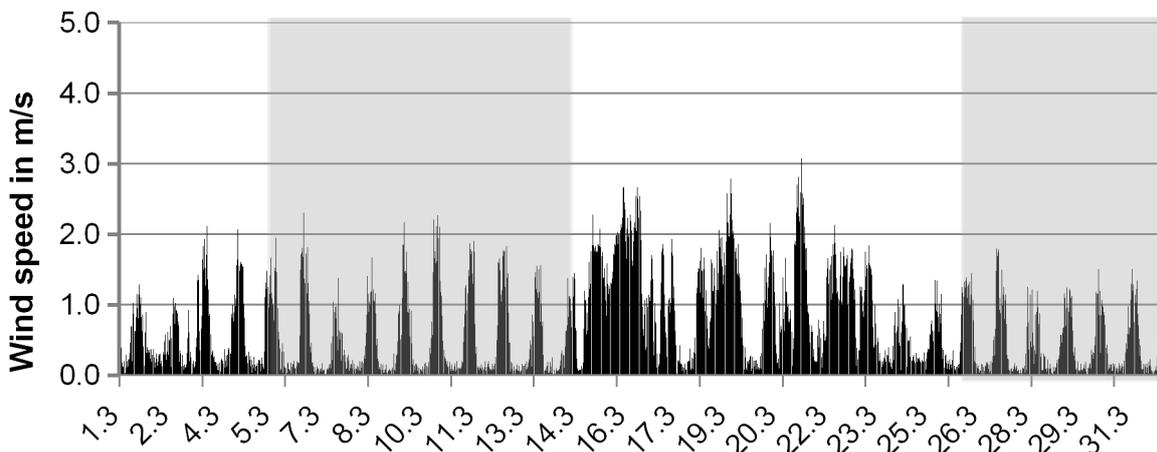


Figure 13: Wind speed course in March 2014

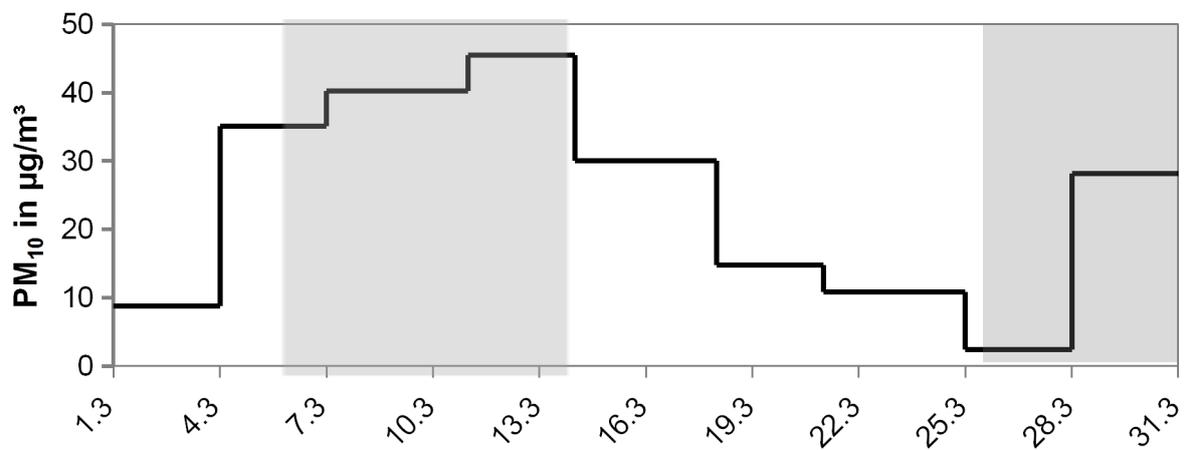


Figure 14: PM₁₀ concentration in March 2014

The inverse behavior between wind speed and pollutants concentrations is approved by the NOx concentrations as shown in Figure 15. When the wind speed shows peaks, relative low NOx concentrations are observed. And when relative low wind speed happens, high concentrations of NOx are observed as peaks. The peaks from both parameters followed each other quite sharply especially during the two inversion periods.

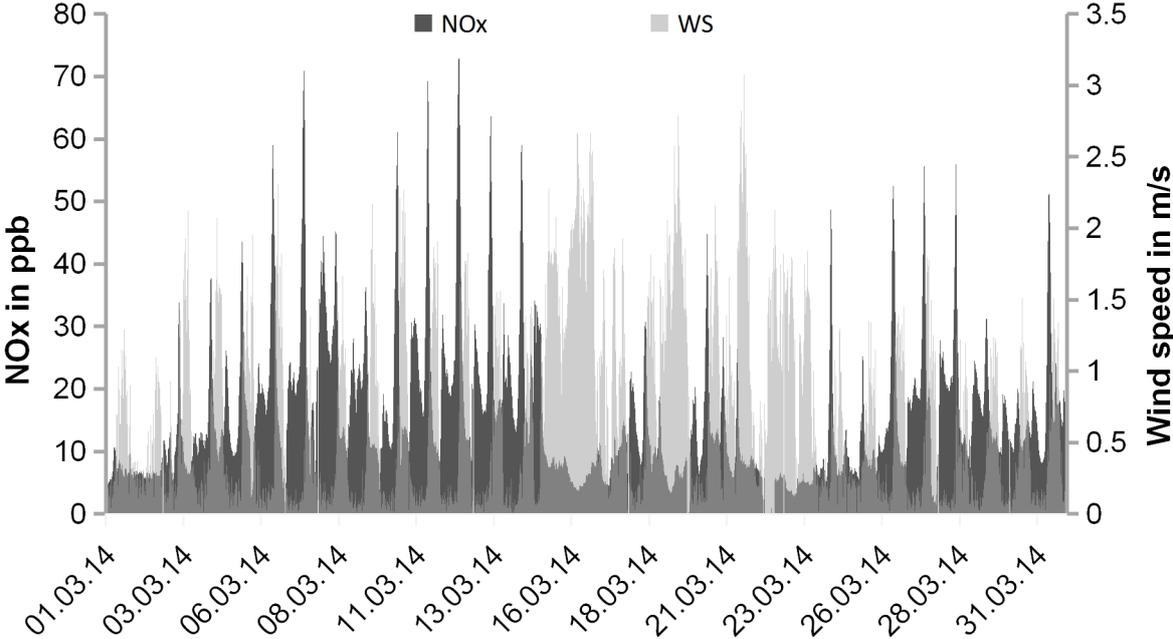


Figure 15: Wind speed (WS) and NOx concentration measured in March 2014

From the discussion above, the local air quality is characterized by fluctuating PM₁₀ concentrations during winter heating periods. The daily average values are mostly below the EU 24h limit value, but air pollutants accumulated and PM concentrations increased significantly during inversion periods.

4.3.2 Particle-bound polycyclic aromatic hydrocarbons

Despite of the fact that PM₁₀ concentrations are mostly below the EU 24h limit value in the study area, wood smoke pollution was still a problem with regards to particle-bound organic compounds, especially PAHs. Based on the literature summary before, analysis of PAHs from our results were carried out in terms of total PAHs, benzo(a)pyrene (BaP) and carcinogenetic potential. Total PAHs are referred to the 16 European or US EPA priority polycyclic aromatic hydrocarbons (Keith, 2015).

In winter 2014/2015, 24 filters (from November 2014 to middle of January 2015) out of 56 filters (collected from November 2014 to March 2015) were analyzed for PAHs. But all these filters are analyzed for other compositions which are discussed in later sections.

4.3.2.1 Total polycyclic aromatic hydrocarbons and benzo(a)pyrene (BaP)

Total PAHs show temporal variations through the two winter periods with two peaks found in December 2013 and in January 2015. The maximal concentration exceeds 50 ng/m³. BaP shows a similar trend like total PAHs with a maximal value of 6.4 ng/m³, corresponding to the highest concentration of total PAHs. The average BaP concentrations for winter 2013/2014 and winter 2014/2015 are 1.8 and 1.2 ng/m³, respectively. In total there are 24 out of 35 filters (66 %) from winter 2013/2014 having a daily average of BaP exceeding the EU annual average limit value of 1ng/m³ for the protection of human health (Directive 2004/107/EC, 2005; Directive 2008/50/EC, 2008). In the winter period 2014/2015, even though only the filters until middle of January were analyzed, still 10 out of 24 (41.7 %) filters are found with a daily average of BaP exceeding the limit value of 1ng/m³.

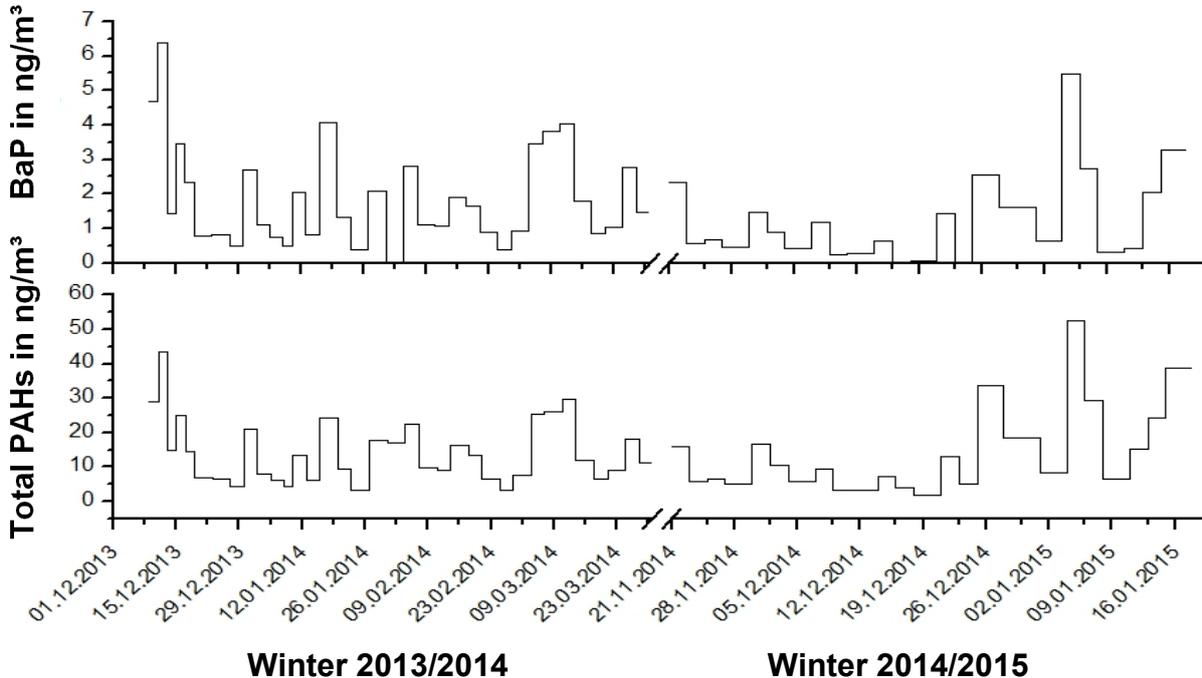


Figure 16: Concentration of total PAHs and BaP from the two measurement campaigns

Correlations between total PAHs and BaP are shown in Figure 17. BaP was not detected in a few samples, which have a concentration of PAHs lower than 10 ng/m³ (with one exception which is lower than 20 ng/m³). For the rest of the filters, when total PAHs show high concentrations, the corresponding BaP concentrations are also high. Correlation coefficients for two campaigns are 0.89 and 0.78, respectively. In winter 2014/2015, the correlation is slightly lower, which might be due to the fact that only 24 filters were analyzed. Nevertheless, high correlations found between BaP and total PAHs imply that BaP could be applied as an indicator for a rough qualitative estimation of total PAHs. The measurement of BaP would be enough to extrapolate exposure to total PAHs in relevant studies if necessary. As BaP is believed to be the most toxic PAH and is a good tracer of the PAH carcinogenic potential, it can be inferred that wood smoke seems to pose a health risk on local residents during winter heating periods. However, BaP is only one of the carcinogenic PAHs and there is still a need for the determination of total carcinogenic PAHs, which will be discussed later in section 4.3.2.2.

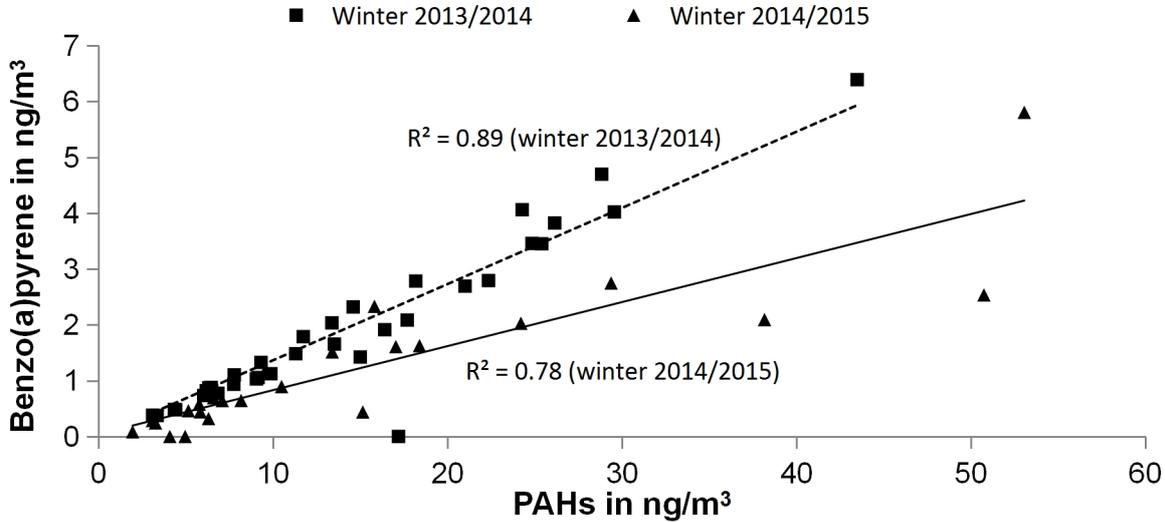


Figure 17: Correlation between total PAHs and benzo(a)pyrene, filter numbers are 35 for winter 2013/2014 and 24 for winter 2014/2015

Monthly average values for these two parameters are listed below. Except for November and December 2014, the measurements in all other months show a monthly average of BaP higher than 1 ng/m³. The reason might be due to the weather conditions in these two months

(relative higher temperature without inversion), which resulted in lower heating activities of the residents. Nevertheless, these results are comparable to the study from Bari et al. (2009) in the same area, which indicates that the local air quality is still polluted by PAHs during the measurement periods of this study.

Table 5: Monthly average concentrations of total PAHs and BaP

Month	Total PAH concentration in ng/m ³		BaP in ng/m ³		
	winter 2013/2014	winter 2014/2015	winter 2013/2014	winter 2014/2015	winter 2005/2006*
November		8.7		1.0	1.5
December	16.3	10.3	2.3	0.8	1.2
January	10.9	23.8	1.6	2.0	3.2
February	12.0		1.2		1.6
March	16.1		2.2		0.6

*Source: Bari, 2009 (values are not accurate numbers but estimated from diagram)

4.3.2.2 Relative contribution of individual PAH and carcinogenic PAHs

The relative contribution of individual PAHs from both measurement campaigns are shown in average values with standard deviations in Figure 18. It is observed that low molecular weight PAHs, which are particle-bound, have a very similar trend for two winters, showing relative contributions smaller than 5 % except for fluorene. A relative high portion of fluorene is found in the samples from winter 2014/2015. Dominant PAHs are also identical within the two winters, which are chrysene, benzo(b)fluoranthene+(k)fluoranthene (BbF+BkF) and benzo(a)pyrene, each accounting for an average contribution over 13 % to the total PAHs. Followings are fluoranthene, pyrene, benzo(a)anthracene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene, which have an average contribution of approximate 10 %. The average relative contributions of phenanthrene and dibenzo(a,h)anthracene are between the ranges of above mentioned low molecular weight and high molecular weight PAHs.

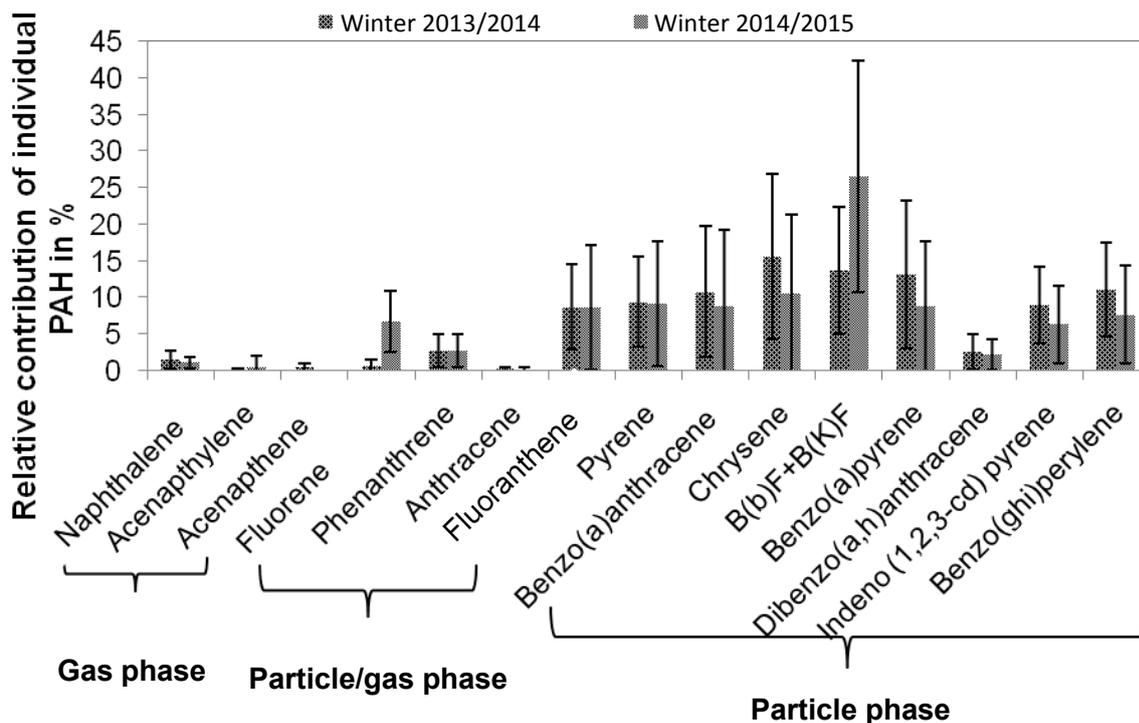


Figure 18: Average values and standard deviations of the relative contributions of particle bound PAHi to total PAHs (PAHi/total PAHs in %)

The relative average concentrations for some individual PAHs show a difference between the two winters. But these differences are very low when taking into account the standard deviations. For example, B(b)F+B(k)F have a difference of about 10 % for the average relative contributions, which becomes smaller than 5 % since the standard deviation in winter 2014/2015 is very high. It is also observed that from fluoranthene onwards, standard deviations are relative high, indicating the wide ranges of these PAHs concentrations found between the samples from the same winter. Nevertheless, these similar trends between two winters indicate that PAHs originated from the same local source.

Some PAHs are recognized to be likely to pose carcinogenic potential on human health and are classified by the International Agency for Research on Cancer (IARC, 1987) into probable (group 2A) and possible (group 2B) human carcinogens as shown in Table 6.

Table 6: Carcinogenic PAHs and their groups

Carcinogenic PAHs	Number of rings	Particle/Gas phase distribution	Humans IARC Group
Naphthalene (NaP)	2	Gas phase*	2B
Benzo(a)anthracene (BaA)	4	Particle phase	2B
Chrysene (Chr)	4	Particle phase	2B
Benzo(b)fluoranthene (BbF)	5	Particle phase	2B
Benzo(k)fluoranthene (BkF)	5	Particle phase	2B
Benzo(j)fluoranthene (BjF)	5	Particle phase	2B
Benzo(a)pyrene (BaP)	5	Particle phase	1
Dibenzo(a,h)anthracene (DBA)	6	Particle phase	2A
Indeno (1,2,3-cd) pyrene (IP)	6	Particle Phase	2B
*only particle phase PAHs have been collected in this study			

1: carcinogenic to humans; 2A: probably carcinogenic to humans; 2B: possibly carcinogenic to humans. Source: International Agency for Research on Cancer (IARC,1987)

As mentioned above, the difference of the relative average contribution from B(b)F+B(k)F is as high as 10 %, but this is, however, compensated by the relative high share of chrysene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene in winter 2013/2014. Therefore, the total carcinogenic PAHs contribute to approximately 65 % of total PAHs whereas other PAHs together add up to around 35 % for two winters (Figure 19 and Figure 20). These high carcinogenic PAHs indicate a health risk on local people during winter heating periods.

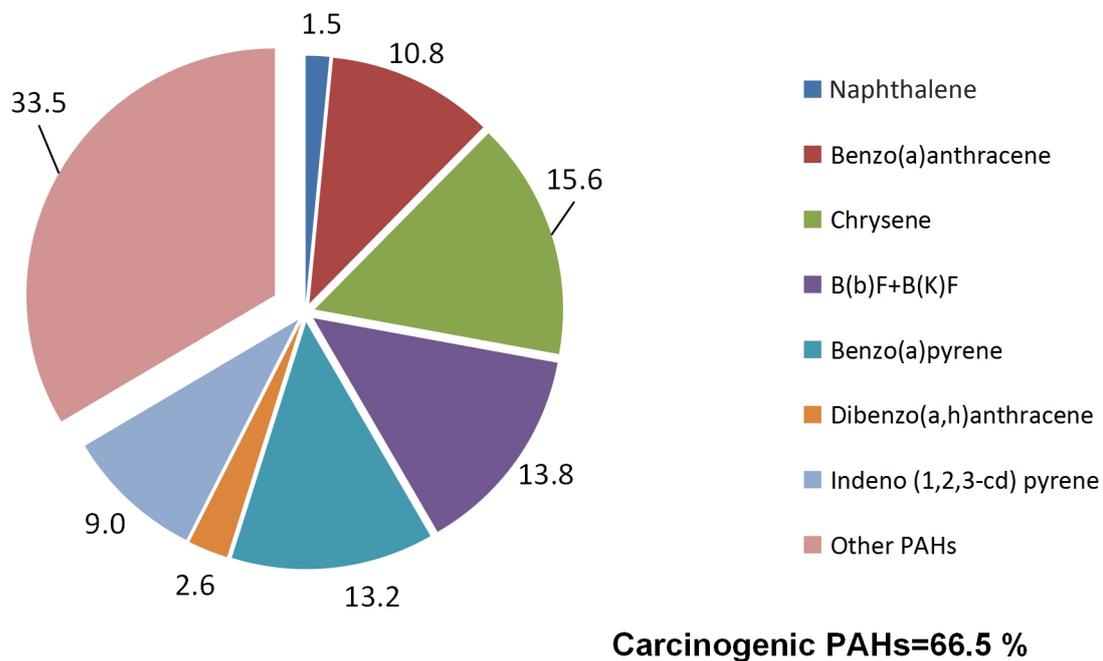


Figure 19: Relative contributions of carcinogenic PAHs in winter 2013/2014 (N=35)

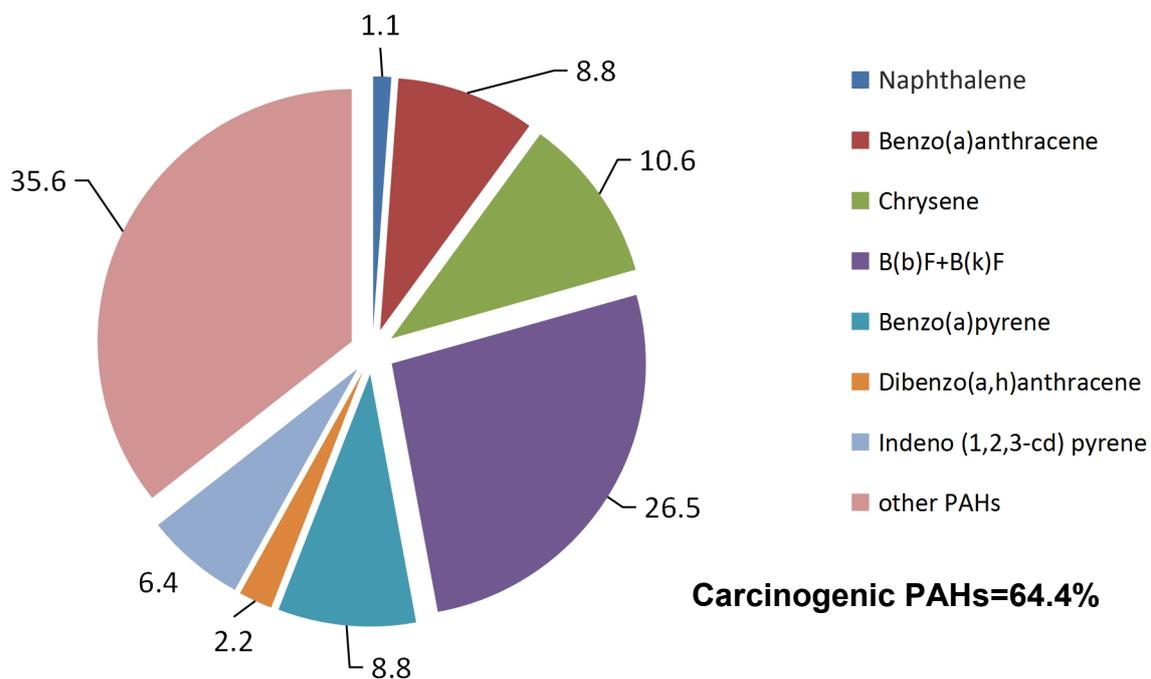


Figure 20: Relative contributions of carcinogenic PAHs in winter 2014/2015 (N=24)

4.3.3 Black carbon

From November 2014 to March 2015, ambient black carbon (BC) was measured continuously using an aethalometer in the investigated area (Model AE 33, Magee Scientific 2014). With this newest model at that time, real time BC concentration and biomass burning BC contribution (BB%) are attained directly with a time resolution of one minute.

In this chapter, the results of BC measurements are discussed in terms of temporal course, diurnal trend and the contribution of biomass burning BC to total BC.

4.3.3.1 Daily and diurnal variation of BC concentration

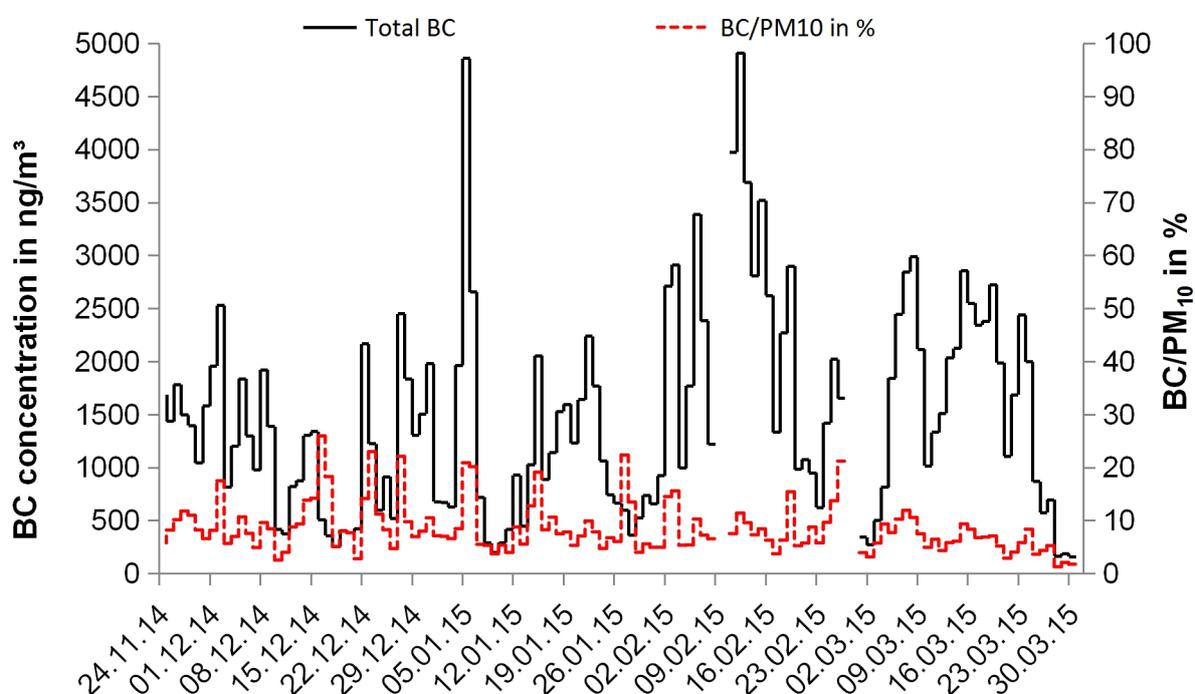


Figure 21: Temporal course of BC concentrations and the ratio of BC to PM₁₀ in winter 2014/2015

The daily average is calculated to show the temporal course of black carbon concentrations, which range from about 500 ng/m³ to nearly 5000 ng/m³, with the dominant range between 1000 and 3000 ng/m³. The average concentration over the whole measurement period is 1500 ± 970 ng/m³ with two peaks reaching almost 5000 ng/m³. The first peak is found in the beginning of January and it is inferred that it might be due to the New Year fireworks. The

second one agrees, however, well with the very high PM₁₀ concentration during this inversion period. The daily average of BC/PM₁₀ ratios shows that BC accounts for 8.5 % of PM₁₀ content, ranging from 1.3 to 25.9 %. This indicates that the BC content is considerable and correlated to PM₁₀ local sources.

These daily BC values are compared to those found from other studies for an assessment of the BC level in the investigated area (Table 7).

Table 7: Comparison of the own measurement results with BC daily average from literature

Site	Daily average BC concentration in $\mu\text{g}/\text{m}^3$, (sampling period)	BC/PM _{2.5} Average (%)	Reference
Dettenhausen, Germany	1.50 ± 0.97 (November 2014 – March 2015)	8.5 (1.3 – 25.9)	This study
In Europe			
Rugštelėškis, Lithuania	0.77 ± 0.52		Pauraitė et al., 2015
Virolahti and Utö, Finland	0.468 ± 0.425 (2006 winter) 0.271 ± 0.348 (2007 winter)	5 and 10	Hyvärinen et al., 2011
Amsterdam and Rotterdam, Holland	0.80 ± 0.54 1.37 ± 0.55 (both region sites in 2013)		Klompaker et al., 2015
Madrid (two sites) and Jaén, Spain	3.70 ± 3.73 traffic urban site 2.33 ± 2.96 urban background 2.61 ± 5.04 rural area (2014 – 2015)	21 20 11 (all in winter)	Becerril-Valle et al., 2017
Barcelona, Spain	3.6 ± 1.8 urban background (July – November 2007)	$38 \pm 15 \mu\text{g m}^{-3}$ (PM ₁₀) $25 \pm 10 \mu\text{g m}^{-3}$ (PM _{2.5})	Pérez et al., 2010
North Kensington and Marylebone, UK	1.9 ± 0.7 Urban Background 7.8 ± 2.7 Road Site (2009)	11 (PM ₁₀)	Reche et al., 2011

Table 7: Comparison of the own measurement results with BC daily average from literature (continued)

Edinburgh UK	1.2 (0.4 – 3.0) , rural site (September 2009 – April 2010)	9	Heal and Hammonds, 2014
Braunschweig, Germany	1.4 – 4.1 (2012 – 2013)		Ruths et al., 2014
Outside Europe			
Xi'an, China	14.7 ± 9.5 (September 2003 – August 2005)	8.3	Cao et al., 2009
Beijing, China	3.7 (Olympic days in 2008)		Wang et al., 2009
Beijing, China	6.8 (2006 – 2011)	8.9	Gong et al., 2019
Beijing, China	5.31 ± 6.27 (urban site) (winter 2015)		Liu et al., 2018
Beijing, China	4.3 (urban area) (2005 – 2013)	6.4	Chen et al., 2016
Shanghai, China	3.8 ± 2.3 (2010) (urban site) 3.3 ± 2.1 (2011)	8.3 (2010) 7.1 (2011)	Feng et al., 2014
Pudong districts, Shanghai, China	3.4 (2008 – 2012)		Wang et al., 2015
Tokyo, Japan	0.249 (winter 2004)	1.12	Uchida et al., 2010
Tokyo, Japan	2.6 (in 2003) 0.6 (in 2010)		Kondo et al., 2012
Ontario, Canada	0.51 – 1.74 (June 2015 – May 2016)		Healy et al., 2017
New York City (NYC), US	1.4 – 2.0 (annual average from 2003 to 2012)	15 – 20 7 – 10	Rattigan et al., 2013

It is observed from the Table 7 that BC in urban areas, especially in megacities in China, is significantly high, which could be mostly attributed to heavy traffic as it is one of the

significant contributors to BC (Baumbach et al., 2016). The same reason could be also responsible for the relative high BC level in Spain compared to other European cities. The results measured in Dettenhausen are comparable to Braunschweig in Germany, Rotterdam in Holland and urban background in North Kensington, and similar to results in Xi'an, Beijing and Edinburgh in terms of contribution to PM.

Diurnal BC trend

Hourly averages of BC are calculated as average diurnal trend to give a sight on the hourly variation of the BC concentration, see Figure 22.

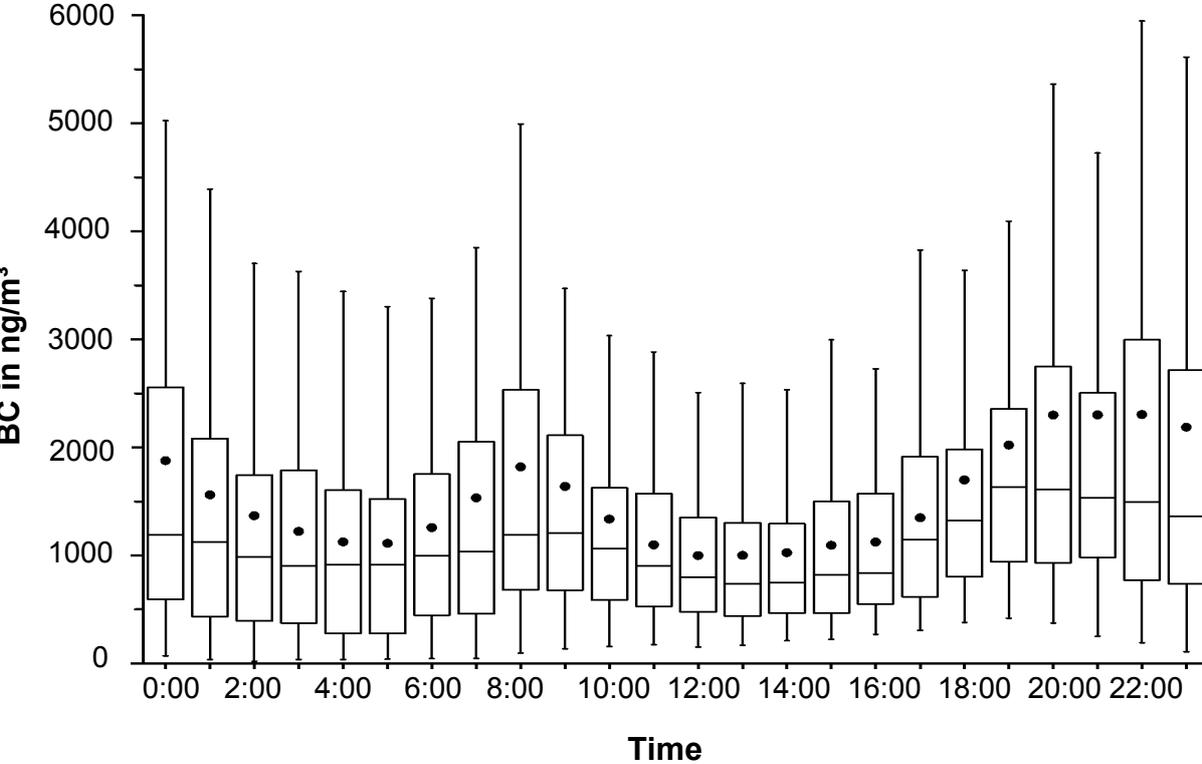


Figure 22: BC average diurnal trend (hourly averages) from November 2014 to March 2015

The hourly average BC ranges from 500 to 2500 ng/m³ and is characterized with a distinct diurnal pattern containing two peaks. The first peak appears in the morning hours, reaching a maximal concentration at 8:00 and ends at 10:00. The second peak found in the afternoon is more pronounced as BC concentration increases continuously to almost a factor of 2 from 16:00 to 20:00, and this very high concentration lasts until midnight. These two peaks can be explained by the combination of source input and meteorological conditions. The emission

source can be associated to the residents' heating behavior, which happens normally in the morning hours and in the afternoon until late evening. This reveals again the impact of residential wood burning on local air quality. Another major contributor to this peak is expected to be traffic emission as diesel engines are the other major source for BC besides incomplete biomass burning at the measurement site. Therefore, the increase of morning BC can be attributed to morning traffic, even though the traffic is generally not heavy in this neighborhood. Another factor that attributes to the morning peak could be the existence of the surface inversion, which favored pollutant accumulation in early morning and is only dissolved by solar radiation when the sunshine is long and strong enough at noon, and the build-up BC concentration gradually is reduced to a lower level of the whole day due to dispersion. In the afternoon, the inversion is formed again after sunset and people spend more time at home during the afternoon and evening, which results in more heating activities with wood burning.

4.3.3.2 Biomass burning black carbon (BB%)

Besides a direct delivery of real-time BC concentration with high time-resolution, the Aethalometer AE33 is also able to apportion sources of BC based on a two-component model from Sandradewi et al. (2008b; 2008c). This model takes into account only two emission sources for BC: biomass burning and fossil fuel burning. The result of BB% shows the contribution of BC from local wood burning. The rest of BC can be attributed to different emission sources depending on local situations, for example, diesel combustion from traffic, residential heating with oil, local background concentrations or input from regional transportation. Detail information about the model could be found in the above cited literature.

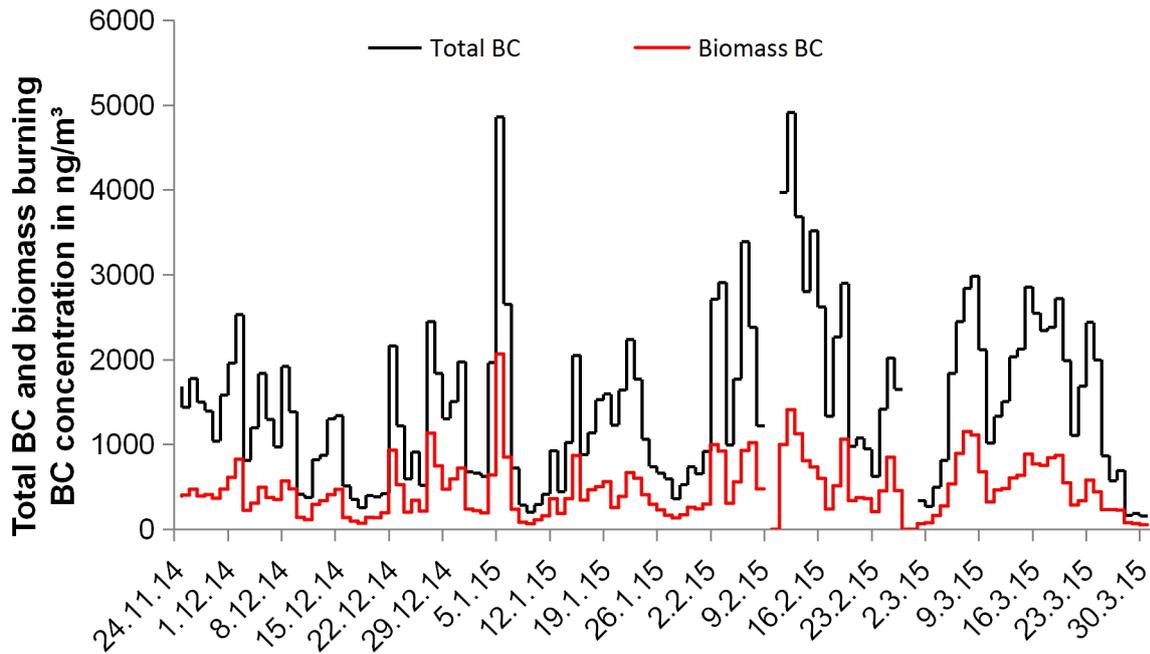


Figure 23: Concentration of total black carbon (BC) and biomass burning black carbon (BB)

From the comparison in Figure 23, the daily average of biomass BC shows a similar temporal course as the total BC and it is nearly half of the corresponding total BC in ng/m^3 . The contribution of biomass burning BC to total BC in percentage is calculated as hourly averages and displayed in Figure 24. The maximum frequency occurred mainly in the range between 20 and 40 %. A detailed calculation suggests that the contribution is between 17.8 and 61.7 %, with an average of 33.3 %, indicating a consistent wood burning effect on the local air quality during this winter heating period. The correlation between biomass burning BC and total BC in Figure 24 (b) shows also a contribution from biomass burning of about 30 %.

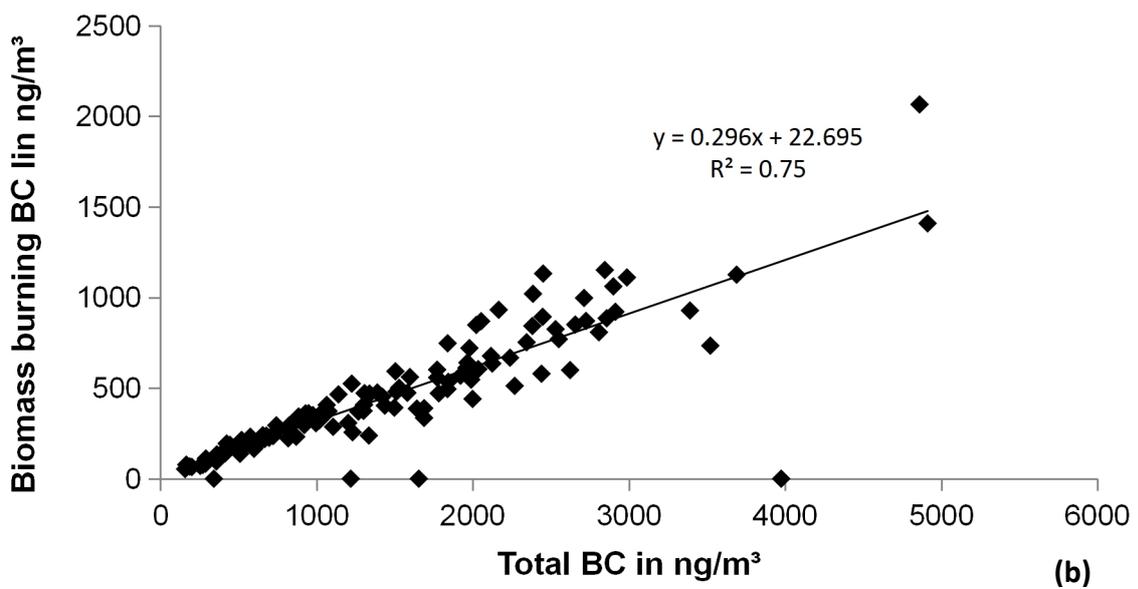
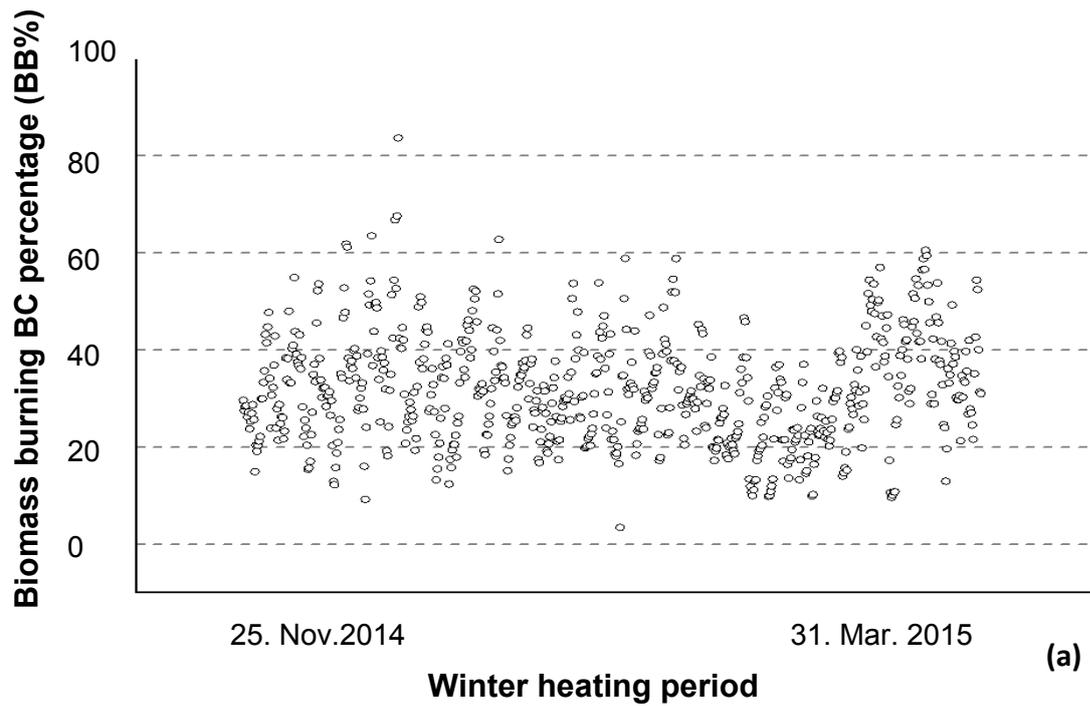


Figure 24: Biomass burning BC percentage (a) and its correlation with total BC (b), based on daily average concentrations in winter 2014/2015

4.3.3.3 BC correlations with gaseous pollutants (CO and NO_x)

CO is an indicator for incomplete combustion from bio-fuel, coal combustion and gasoline vehicles during cold start. NO_x is considered as an indicator for traffic emission. Therefore, the correlations between BC and these two parameters are also analyzed for a rough estimation of BC origin. Data of CO, NO_x and BC are averaged into hourly values as shown in Figure 25 and Figure 26.

It is shown in Figure 25 that BC and CO vary similarly during this period with a significant high correlation coefficient of 0.83, indicating that BC and CO emissions are likely from the same source. With regards to the characteristics of the measurement site, CO emission from coal combustion can be eliminated and the major emission source of CO is more likely to be biomass burning. Therefore, the high correlation between BC and CO is an indicator for biomass burning as origin of most of the BC. A similar trend is observed between BC and NO_x but with a lower correlation coefficient of 0.71. As mentioned above, NO_x is also traffic-related. However, the measurement site is near a road inside a pure residential area where only little traffic (mostly caused by the residents) could be observed. Therefore, local traffic seems not to be a very important emission source for NO_x. Instead, there are some other potential emission sources, for example, oil firings and remote pollutants transport. This means, a certain amount of NO_x can be also attributed to these potential sources instead of biomass burning. To summarize, biomass burning has a considerable contribution to total BC during the measurement period in this study. This agrees well with the result of biomass burning BC (BB%) as discussed in Chapter 4.3.3.2 .

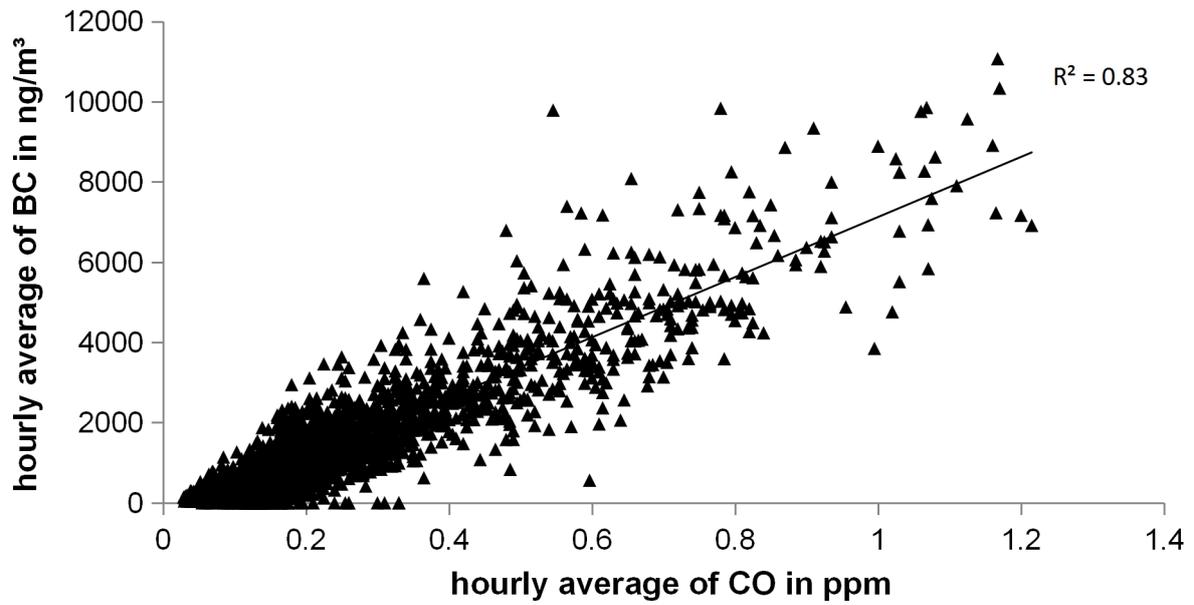


Figure 25: Correlation between hourly average values of BC and CO in winter 2014/2015

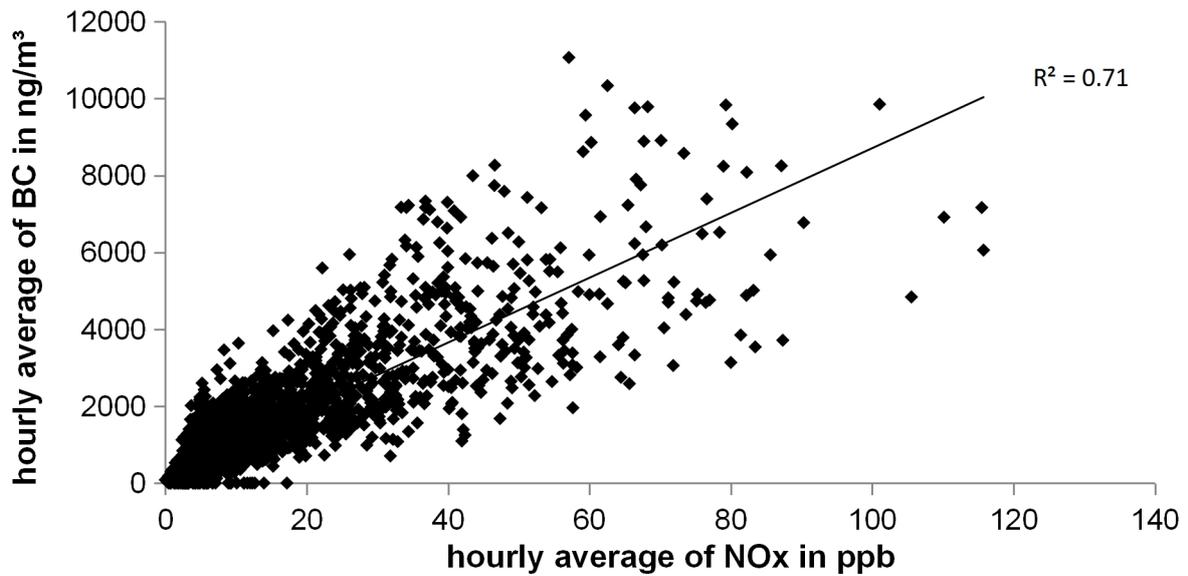


Figure 26: Correlation between hourly average values BC and NOx in winter 2014/2015

4.3.3.4 BC correlation with PM₁₀

The correlation between BC and PM₁₀ is not as high as that with gaseous pollutants CO and NOx, but the trends agree very well with each other, especially for the lowest and highest values (Figure 27). This demonstrates a relative constant share of BC in PM₁₀, which can be

estimated to be about 10 %. This should be due to the consistent contribution from the same emission source of local PM₁₀ and BC.

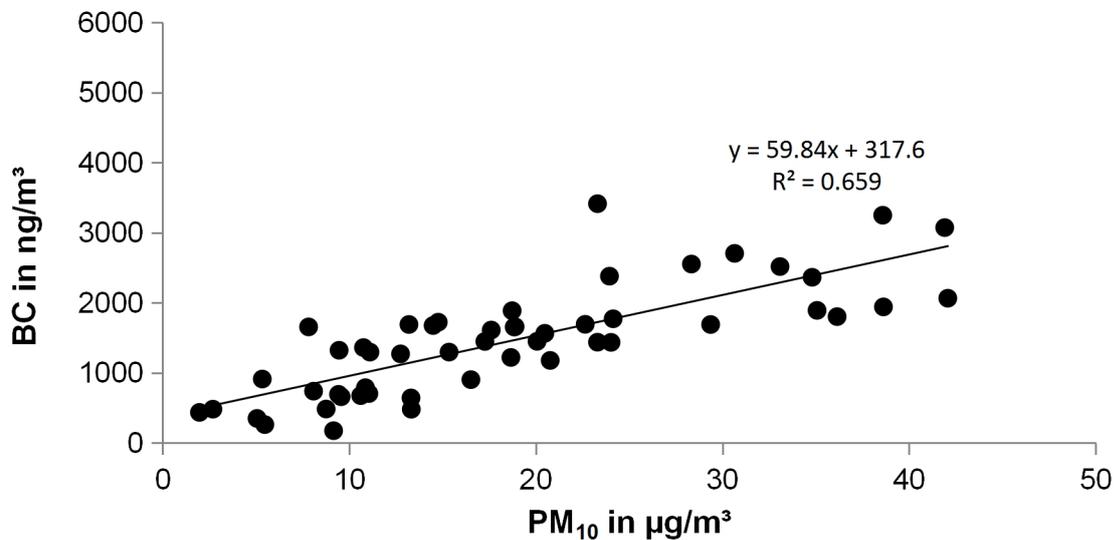


Figure 27: Correlation between daily averages of BC and PM₁₀ in winter 2014/2015 (number of PM samples: 56)

4.4 Measurement of levoglucosan in ambient PM₁₀

As a unique tracer for wood burning PM, levoglucosan in ambient air indicates PM pollution from residential wood burning during heating periods.

4.4.1 Levoglucosan concentration and its content in PM₁₀

The temporal course of levoglucosan concentration determined from each PM sample is shown in Figure 28. Levoglucosan is detected from all PM samples except one filter collected in December 2014. The concentration fluctuates within a wide range between 7 and 1550 ng/m³. The average concentrations for two winter periods are 323 ng/m³ and 344 ng/m³, respectively. This reveals the consistent input of wood burning PM to ambient air. The same trend is also observed for the ratio of levoglucosan to PM₁₀, which presents the share of levoglucosan in PM mass. These ratios are in winter 2013/2014 within a relative narrow range with an average ratio of 1.9 %, while the ratios in winter 2014/2015 show profound variations with an average ratio of 2.7 %. High ratios indicate high mass fraction

of levoglucosan in PM_{10} content, but its interpretation should be combined with the levoglucosan concentrations. For example, there are high ratios corresponding to low levoglucosan concentrations in winter 2014/2015, which indicate wood burning is the major contributor to PM_{10} . A relative low ratio is also observed at high levoglucosan concentration, suggesting other emission source for ambient PM. Nevertheless, a substantial share of levoglucosan to ambient PM_{10} from residential wood combustion is found in winter 2013/2014 and winter 2014/2015.

These results are compared to other measurements in Europe especially in Germany found in literature (Table 8). Some measurements in these literatures cover a long measurement period and include summer seasons, but only results from winter season are compared for since only winter periods are relevant for wood burning and are covered in this study.

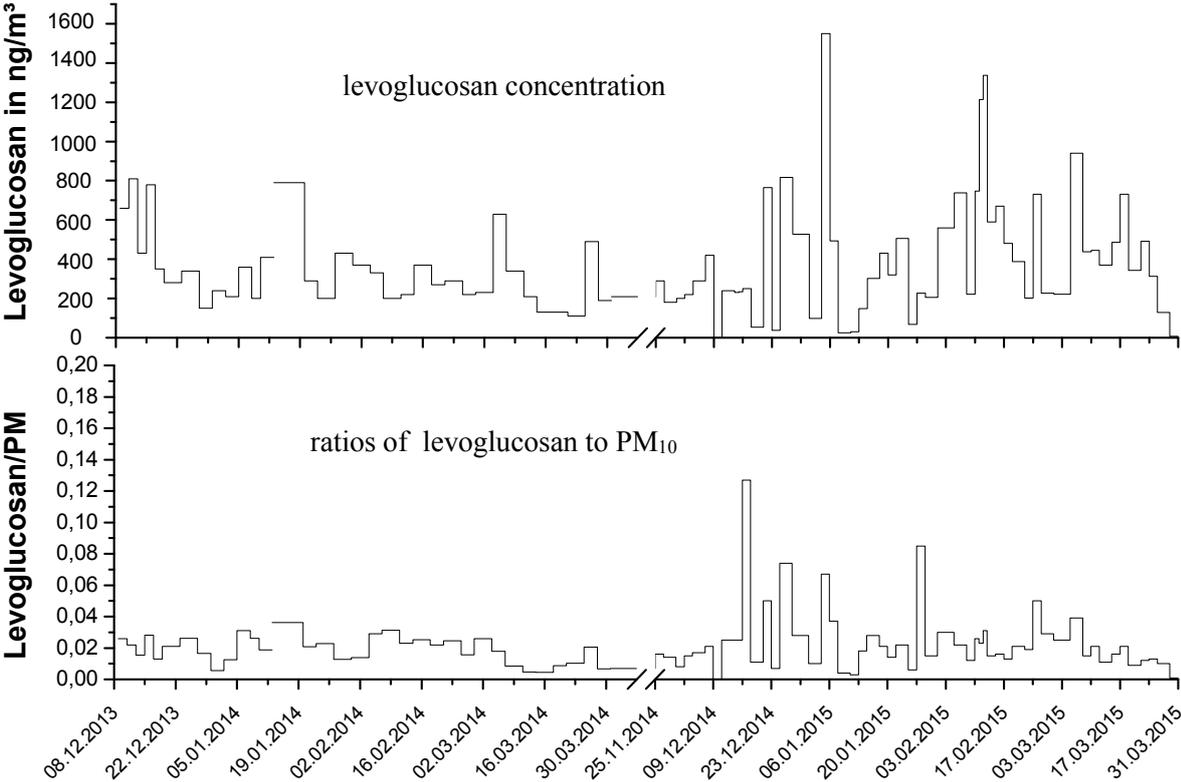


Figure 28: Temporal course of levoglucosan concentration (above, in ng/m^3) and its content in PM_{10} (below) in two winters in the residential area

With average values of 323 and 344 ng/m³, levoglucosan concentrations in this study are comparable with the levels found in Augsburg and NRW (Pfeffer et al., 2013). The corresponding ratios between levoglucosan and PM₁₀ are, however, higher than those found at these two sites (Augsburg 1.0 % and NRW 1.0 - 1.7 %). The reason for that is that there are other PM₁₀ sources, especially the traffic, whereas wood burning may be the most important PM₁₀ source in the residential area of Dettenhausen. Bari has found, however, a two time higher levoglucosan concentration of 806 ng/m³ in winter 2005/2006 in the same area. Levoglucosan levels reported from other sites in Europe are also very similar to the results of this study. Very similar level in urban traffic and urban background but a relative lower suburban background concentration is observed in Tuscany, Italy. The high concentrations of levoglucosan proved a more intensive wood fire for domestic heating (Giannoni et al., 2012). In Austria, Graz reports a relative high value of 680 ng/m³ compared to Vienna and Salzburg (Caseiro et al., 2009). These results show a general pollution situation resulted from residential wood combustion across these European regions and wood smoke should be controlled.

Table 8: Comparison of levoglucosan concentrations in literature

Sampling site	Levoglucosan concentration (ng/m ³)	Levo/PM ₁₀ or (Levo/PM _{2.5})	Sampling period	Reference
Dettenhausen	323 (111-806)	1.9 % (0.5-3.6 %)	Winter 2013/2014	This study
Dettenhausen	344 (0-1550)	2.7 % (0-12.7 %)	Winter 2014/2015	
Dettenhausen	806 (35-3223)	N/A*	Winter 2005/2006	Bari, 2009
CARBOSOL Sites	6.6-1290	N/A	Winter period 2002 - 2004	Puxbaum et al., 2007
Duisburg Prague Amsterdam Helsinki		1.6 (0.71-2.5) 4.4 (3.3-6.3) 1.3 (0.52-2.4) 2.0 (1.3-3.0)	2002 - 2004	Saarikoski et al., 2008
Vienna, Austria Salzburg, Austria Graz, Austria	220 300 680	N/A	Winter period 2004	Caseiro et al., 2009
Augsburg	328 (37-939)	1.0 %	Heating period 2006/2007	Bayerisches Landesamt für Umwelt, 2009
	421 (29-1922)	1.1 %	Heating period 2007/2008	
Tuscany, Italy urban background urban traffic suburbanbackground	371 355 117	2.0 1.1 1.6	Mar 2009 - Mar 2010	Giannoni et al., 2012
7 stations in Flanders, Belgium	(median) 138-640	N/A	Feb 2010- Feb 2011	Maenhaut et al., 2012
NRW	400-700	1.0-1.7 %	Nov 2011	Pfeffer et al., 2013
Tuebingen	300-1000	N/A	Jan, Feb and Dec in 2015	LUBW, 2016

*N/A: not available

4.4.2 Correlations with other pollutants

Correlations between levoglucosan and other PM-bound compositions or other air pollutants can be used to estimate wood burning contribution to these ambient pollutants.

4.4.2.1 Levoglucosan and PM₁₀

Figure 29 shows the correlations between levoglucosan and PM₁₀ in two winters. In general, levoglucosan increases with increasing PM₁₀. However, a certain amount of PM samples present relative low levoglucosan at very high PM₁₀ concentrations, which indicates other emission sources of PM₁₀ besides wood combustion. There are also some samples characterized with very high levoglucosan at relative low PM₁₀ concentration, which imply major PM input from wood burning. These observations agree well with the considerable fluctuation and discussion of Figure 28. Relative poor correlations between levoglucosan and PM₁₀ concentration are found for two winters (Figure 29), indicating residential wood burning is not the single emission source of local PM₁₀.

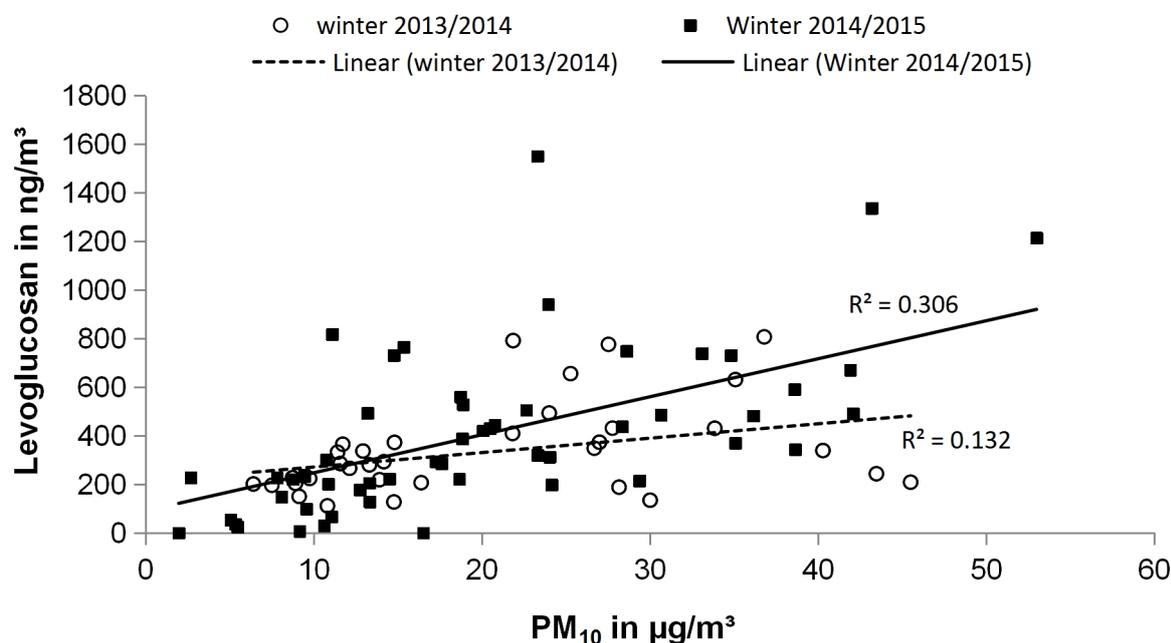


Figure 29: Correlations between levoglucosan and PM₁₀ in ambient samples of the residential area in Dettenhausen (based on daily average values)

4.4.2.2 Levoglucosan and BaP

The correlations between levoglucosan and BaP for winter 2013/2014 and winter 2014/2015 are shown in Figure 30. It can be seen that the correlation for winter 2014/2015 is relative high, which proves that BaP found in the ambient PM₁₀ samples are highly correlated to wood combustion emissions.

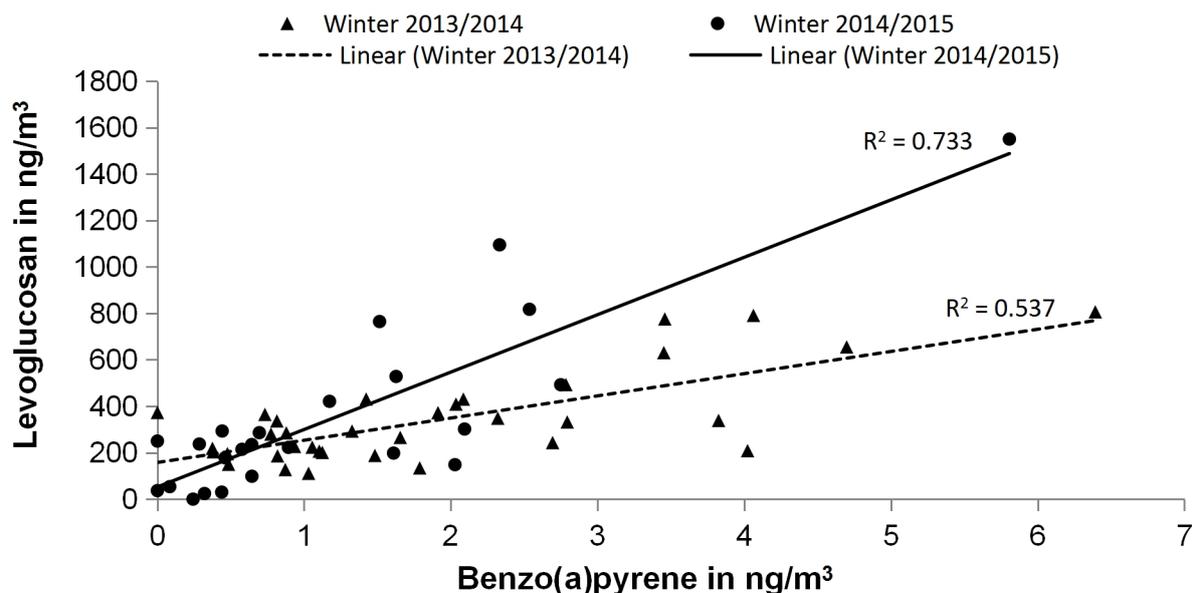


Figure 30: Correlation between levoglucosan and BaP in winter 2013/2014 (filter number: 35) and 2014/2015 (filter number: 24)

4.4.2.3 Levoglucosan and BC

A regression coefficient of 0.587 is found for levoglucosan and total BC (Figure 31), which indicates wood combustion is responsible for about 60 % of the total ambient BC. Since levoglucosan is a unique tracer of biomass burning, theoretically, a higher correlation coefficient of 0.745 is found between levoglucosan and biomass burning BC, but not as high as expected, for example, 0.9 or an even higher value. The reason might be due to the assumption of the calculation model for biomass burning BC, which assumes only two emission sources for total BC, but in reality there are more potential sources for example, oil firing for residential heating. Nevertheless, this ratio provides a rough estimation of the

levoglucosan concentration, which is important for measurement sites where BC measurements are carried out but no levoglucosan data are available.

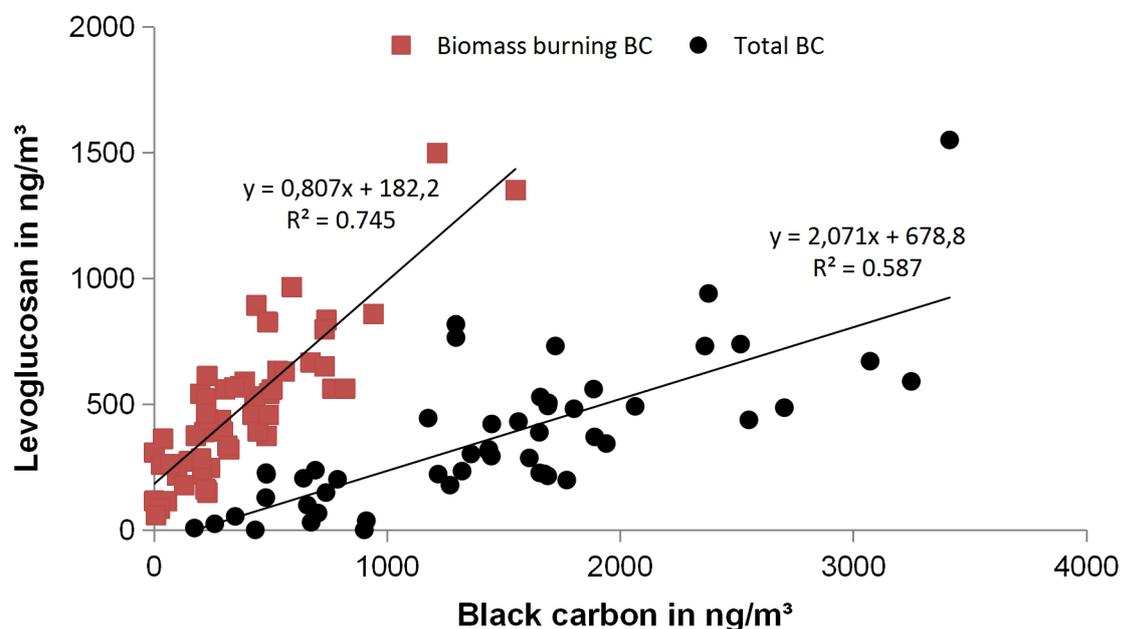


Figure 31: Correlation between levoglucosan and black carbon (total BC and biomass burning BC, based on daily average values)

4.4.2.4 Levoglucosan and organic carbon and elemental carbon (OC/EC)

As mentioned before, due to the limited capacity of the Sunset equipment in laboratory (Sunset Laboratory Inc., 2019), only 10 loaded filters are analyzed for OC/EC and the results are shown in Figure 32. These analyzed filters were collected during two inversion periods, one of which was in February 2015 (12.02.2015 - 19.02.2015) and the other was in March 2015 (13.03.2015 - 23.03.2015). Results from these ten filters show that PM_{10} concentrations are higher than $30 \mu\text{g}/\text{m}^3$ with average concentrations of $42.6 \mu\text{g}/\text{m}^3$ and $36.2 \mu\text{g}/\text{m}^3$ for February and March, respectively.

As discussed in Chapter 2.4 relating BC definition, individual definitions of OC/EC are empirical and must be correlated to the specific determination methods. The results presented here are referred to OC/EC determined using a sunset equipment with NIOSH method (Sunset Laboratory Inc., 2019) at LANUV. The OC/EC results in Figure 32 are the

ratios between OC and EC (left) and their correlation (right). These are briefly discussed together with their correlations with levoglucosan below.

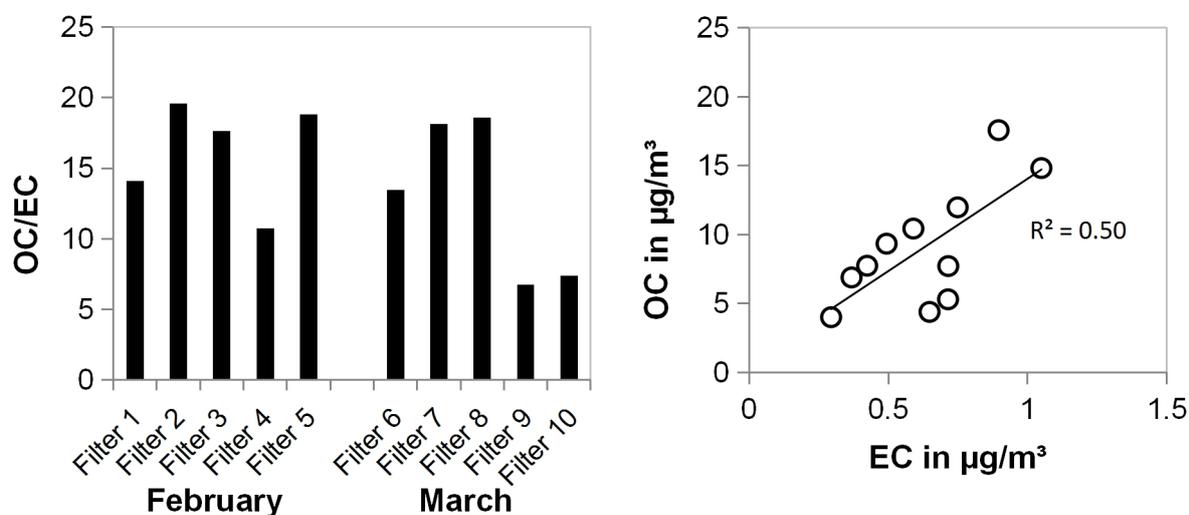


Figure 32: Ratios between OC and EC (left) and their correlation (right)

Both fossil fuel and biomass combustion result in OC and EC formation but EC is more considered as a "good" tracer for fossil fuel emission (Baumbach et al., 2016) while OC has various sources. Based on the situation in this residential area, fossil fuel emissions are related to traffic exhaust and residential oil firing. However, this study did not cover the measurement of OC from residential oil firing and how far this affects the local OC is unknown. There are also scarce relevant studies in literature regarding OC from residential oil firing, which might be due to the fact that PM emission from oil firing is very low (McDonald, 2009). Instead, some early studies show that biomass burning is the largest contributor to global primary OC and EC (Bond, 2004). Nevertheless, oil firing is dominant in residential heating in the residential area in Dettenhausen during winter heating periods and it can be another potential source besides residential wood burning for the measured OC.

Emission ratios between OC and EC and their correlation enable a rough apportion of their sources. In general, low OC/EC ratios indicate high contribution of traffic and high ratios should be a sign for high contribution from biomass burning, as reported ratios from other studies for vehicle exhaust (2.5 to 5.0) and biomass burning (3.8 to 13.2) (Schauer et al., 2002; Zhang et al., 2007).

With respect to the results in Figure 32, OC is almost 20 times higher than EC for half of the samples, with the lowest ratios of 5 for two samples from March 2015 (Figure 32, left side). This indicates a prevailing influence from residential wood burning on the PM samples. A medium coefficient of 0.50 for the selected 10 samples (Figure 32, right side) suggests that OC is not very strongly correlated to EC. But OC has a strong correlation with levoglucosan (Figure 33). This correlation has been used to evaluate the contribution from biomass burning to aerosol OC during winter in studies (Puxbaum et al., 2007; Caseiro et al., 2009). A correlation coefficient 0.84 from the chosen samples suggests that a large fraction of OC could be generated and emitted from wood burning along with levoglucosan during this inversion period. This result agrees well with the finding from Jung et al. (2014), who also found a coefficient of 0.87 between levoglucosan and OC ($\mu\text{g C}/\text{m}^3$). The physical meaning of the offset is the OC input from other sources when levoglucosan is not found.

In contrast to OC, EC does not so strongly correlate with levoglucosan. However, wood burning seems to still account for a certain portion of the EC, when the other half of EC can be attributed to oil burning and traffic emission in this residential area.

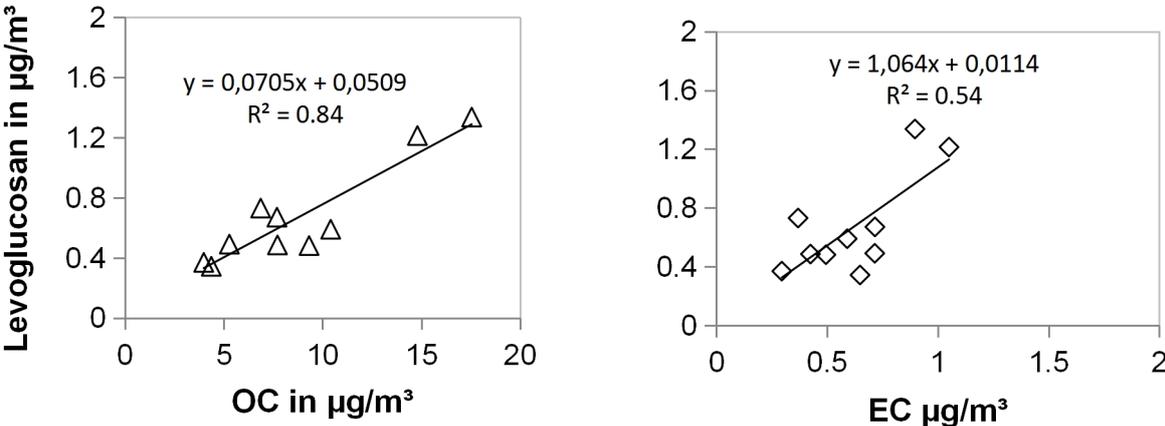


Figure 33: Correlation between levoglucosan and OC (left) and EC (right) for filters collected during inversion periods in February 2015 and March 2015 (according to Figure 32)

The discussion here is a rough estimation due to the limited available data. A deeper discussion regarding the origins of OC and EC should be considered in future studies when the analysis of a large numbers of PM samples is available.

All the above discussed correlation coefficients are listed in Table 9. Because OC/EC results are from samples collected in February and March 2015, the correlations between levoglucosan and PM₁₀ and BC are also calculated for these two months. It can be seen that the correlation coefficient of 0.60 between levoglucosan and BC is a little bit higher than that for the whole winter (0.49), indicating BC pollution is correlated to wood burning during this period due to inversion weather conditions.

Table 9: Correlation coefficients between levoglucosan and other pollutants

	PM ₁₀	BaP	BC	OC	EC	Source
Levoglucosan	0.13	0.54				Winter 2013/2014
	0.31	0.73	0.59			Winter 2014/2015
	0.31	-	0.60	0.84	0.54	February and March 2015

4.5 Case study: is indoor air polluted by wood burning?

With respect to the discussion above, it is concluded that ambient air quality is affected by wood combustion emissions especially under inversion weather conditions when the local flue gases are concentrated. Taking into account some occasions for wood smoke emitting into the room, for example during stove door opening for ignition and fuel replenishment, it leads to the concern about affected indoor air quality with regards to wood burning products. Moreover, there would be also a possible leakage of flue gas due to inappropriate installation of the wood stove. On the other side, indoor pollution could also be affected by ventilation, during which pollutants with higher concentration from outside penetrate into the room through windows or door. Nevertheless, there is increasing awareness and concern about indoor air pollution and it is necessary to investigate if operation of wood-burning could have obvious negative effects on the indoor air quality especially during inversion periods.

4.5.1 Objectives and tasks

Specific objectives of the indoor measurement are to quantify indoor concentrations of various wood burning products and to study the relationship between indoor and outdoor pollutant concentrations, which is depicted as indoor-to-outdoor ratios of specific pollutants. To investigate this, a short-term measurement campaign was planned with the main focus on measurements of PM₁₀, CO and BC pollution indoor. Based on measurements of air pollutants and chemical analysis of collected PM samples inside a house, this case is expected to evaluate indoor air quality when wood burning in stove is presented and to find out if wood burning activity is a serious potential source for indoor air pollution.

4.5.2 Site characterization

The measurement was conducted in a common residential house inside the investigated area in this study. This house is mainly surrounded by other houses or by greenery area in neighborhoods. A side street is in front of the door with relative low traffic flow. The effect from traffic emissions is estimated to be very limited. Inside the house are floors and the first floor includes a living room and a kitchen. Measurements were carried out in the living room, which is square with an area of ca. 20 m². A wood stove is installed in the living room (see Figure 34).

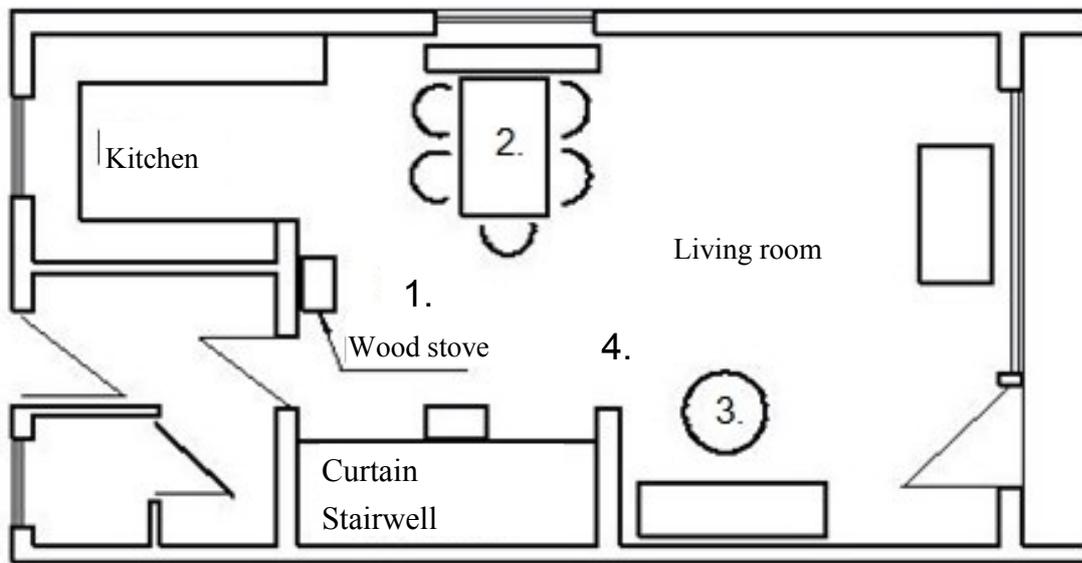


Figure 34: Drawing of floor plan of living room (1 is ca. 0.5 m away from the stove, 2 is a dinner table and 3 is a sofa table. These are the three measurement points for room temperature, relative humidity and CO₂. PM₁₀ sampling head is located at 4) (adapted from Grabner, Student study, 2015)

4.5.3 Sampling program, measurement techniques and experimental conditions

Measurements were carried out for 4 days during the second week in February 2015. Concentrations of combustion pollutants, PM₁₀, BC and CO were measured during normal wood firing activities in a wood stove from the householder. Meanwhile, CO₂, temperature and relative humidity were measured (Grabner, Student study, 2015).

PM₁₀ was measured indoor and outdoor simultaneously, with both continuous and discontinuous methods. For discontinuous measurement, integrated samples were sampled by two low volume samplers, one located in the middle of the living room with a certain distance from the stove (see Figure 34). The other was placed on the top of garage which locates on the left side of the house. The sampling started when the wood burning was started in the morning and lasted for a period between 24 h and 72 h. Continuous PM monitoring was carried out in parallel to attain a temporal course of PM so that the difference between "with wood combustion" and "without wood combustion" in the house could be identified. The indoor background concentration of PM₁₀ was continuously

measured when wood combustion was absent. Concentrations of BC, CO and CO₂, temperature and humidity inside the room were also continuously monitored during the wood burning and up to the evening. A Portable Aerosol Spectrometer and Dust Monitor (Grimm 1.108, GRIMM Aerosol Technik GmbH & Co. KG, 2019) were applied for continuous monitoring of PM, while other measurement techniques are the same as those applied in ambient measurement as listed in Table 3.

Before each experiment, the living room was first ventilated for at least 10 minutes. After that, windows and doors were closed. Curtains were set up as obstacles for ventilation control at stairs from the first floor to the basement and at stairs to the second floor. Other possible emission sources were strictly avoided during the measurement: no central heating by burning of light oil, no smoking event and no activities inside the kitchen. The numbers of occupants inside living room were limited to 3 people during the measurements.

The weather during the measurement days was sunny and windless, with ambient temperature between 0 and 4 °C for most of the time. There were serious inversion conditions during night over the whole measurement week, which could be characterized by meteorological measurements.

Firing of wood was conducted by the homeowner who followed his usual behavior without taking any instruction of experimental protocol, which represented a ‘real-life’ situation. Nevertheless, the wood combustion behavior from the participator was recorded in terms of time and main activities.

4.5.4 Indoor air measurement results under inversion weather

The weather conditions in this one week are presented in terms of temperature and wind speed in Figure 35. It is obvious that the temperature from 10. February onwards depicted a typical inversion pattern as already discussed before in Chapter 4.3.1. In the evening, the temperature decreased dramatically and the wind speed became very low, and the inversion was formed. During the day, the temperature increased significantly and dissolved the inversion, causing air turbulence and subsequently higher wind speed.

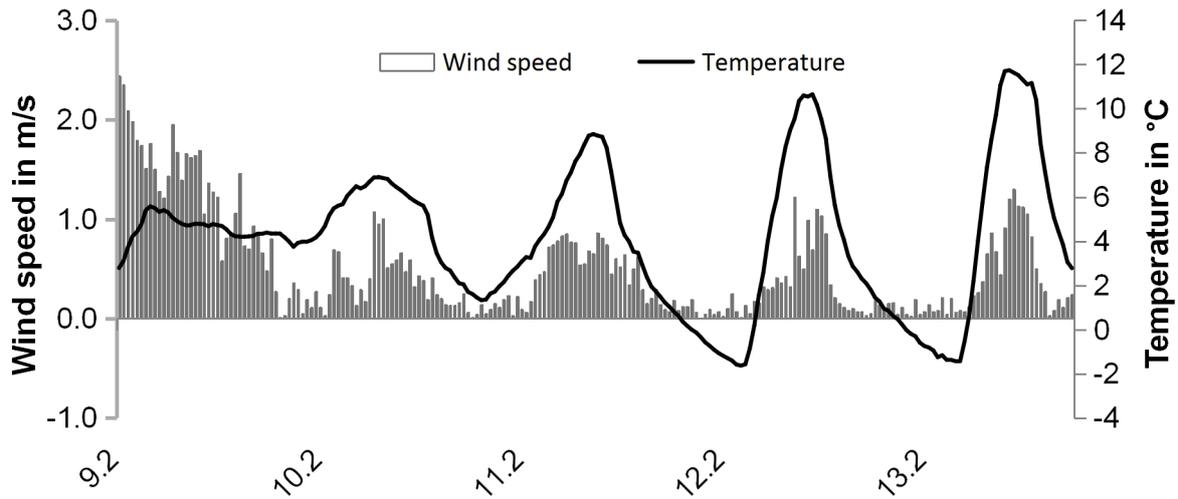


Figure 35: Wind speed and temperature (one week in February 2015)

A direct correlation between meteorological parameters and pollutants is not discussed here. Instead, results from indoor continuous measurement of PM₁₀, CO and BC are first discussed to show the effect from wood burning under inversion weather. After that, indoor and outdoor levels of PM₁₀ and levoglucosan are compared, respectively.

4.5.4.1 Indoor concentrations of wood combustion products - PM₁₀, BC, CO and CO₂

Results from one measurement day are depicted in Figure 36 and Figure 37 in terms of indoor PM₁₀ and BC, CO and CO₂ concentrations, respectively.

As a typical incomplete combustion product, CO found in indoor air is attributed to the existing wood combustion. Indoor BC originates also from the combustion process or from penetration of outdoor air. CO₂ is not a pollutant but its profile could reveal information about the combustion process and possible leakage of flue gas. Its content was measured at several sites in the living room (see Figure 34). PM₁₀ has several potential emission sources but it is easy to identify the contribution from wood burning since indoor activities like cooking and smoking were excluded and the background concentration was measured.

By referring to the protocol, some points on the timeline in Figure 36 are marked with black arrows, which were the time points when firing behavior was conducted, with the first arrow as ignition and the rest as refueling. Firing was ended at 13:00 and the measurements of CO

and CO₂ stopped at this time point but the measurements of PM₁₀ and BC continued for two hours more. It can be recognized that the ignition and the fuel replenishment caused obvious peaks of pollutants in terms of CO and BC, but these are not all recognized in the PM₁₀ profile, which might be due to less sensitivity of the PM instrument. CO₂ increased gradually, which could be partially attributed to the breathing of the persons indoor. Nevertheless, some high peaks of PM₁₀ are observed in the profile (Figure 36), which might be the obvious response due to a relative long opening of the stove door. It can be seen that the operation of fuel refreshing is the cause of gaseous and particulate pollutants escaping into the room.

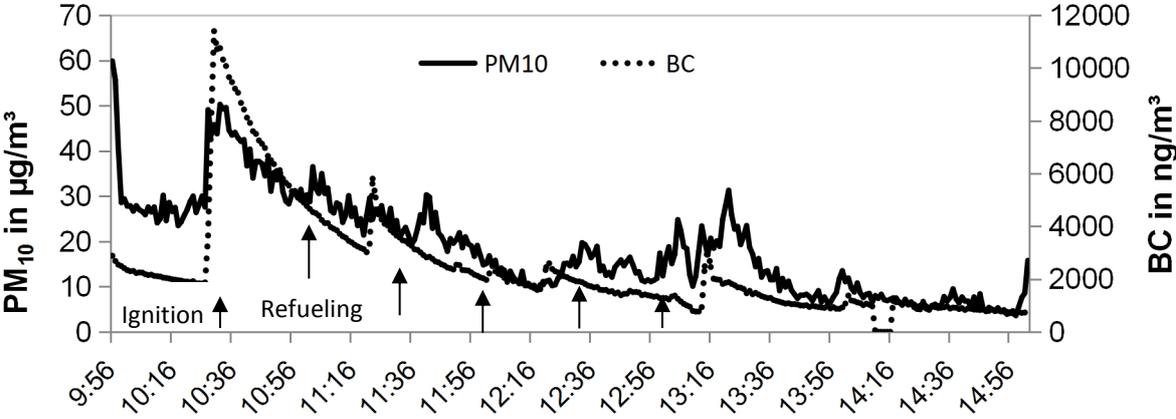


Figure 36: PM₁₀ and BC concentrations during wood firing indoor on 10 February, 2015

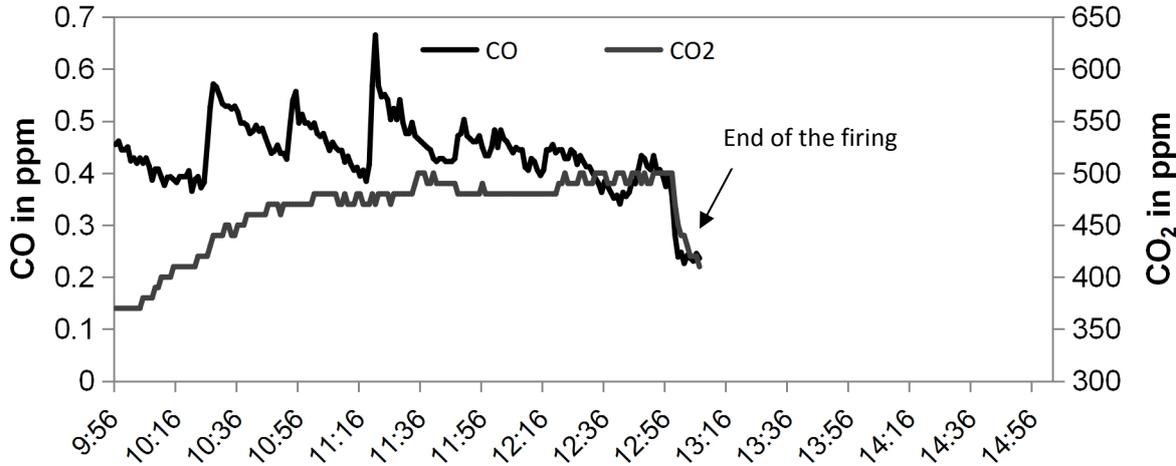


Figure 37: CO and CO₂ concentrations during wood firing indoor on 10 February, 2015

4.5.4.2 Results of continuous outdoor measurements

Continuous outdoor measurements included PM₁₀ on the roof of the garage. CO and NO_x measurement results are attained from the measurement van. PM₁₀ is calculated as half hour average concentration (see Figure 38) and its correlation with CO and NO_x is shown in Figure 39.

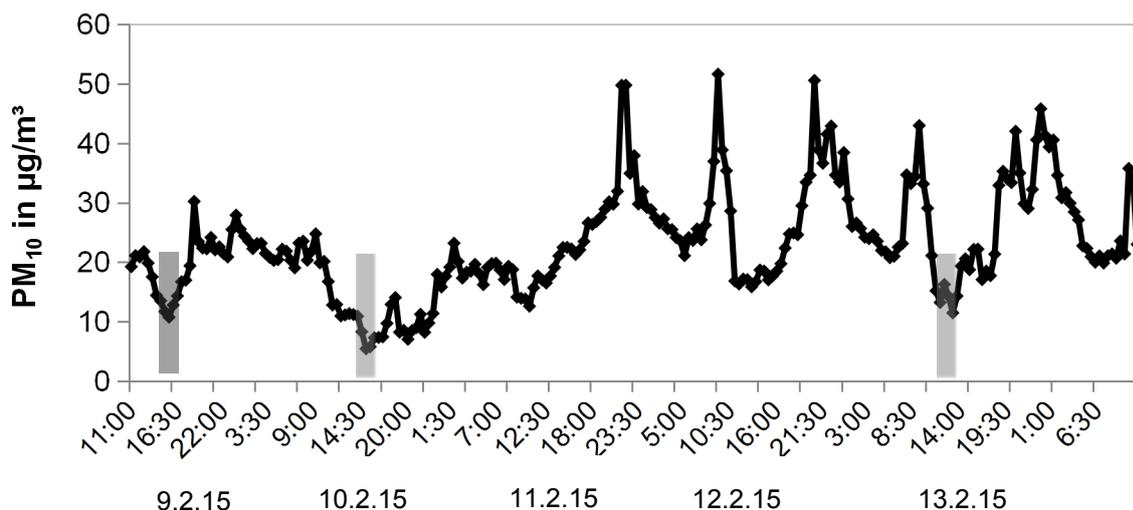


Figure 38: Half-hour average concentration of PM₁₀ measured on the roof of the garage

The temporal profile of PM₁₀ in Figure 38 shows several very low concentrations, which mainly happened in the afternoon as highlighted with the grey bars, corresponding to the absence of heating behavior at this time. Meanwhile, concentration peaks as high as 50 µg/m³ appeared also several times, some happened during the night (from 20:30 to 23:30) and the others occurred in the morning hours (9:00 to 10:00). These morning and evening peaks agreed again very well with the residents heating behavior. These PM₁₀ concentrations have a correlation coefficient of 0.367 with NO_x and a slightly lower value with CO (Figure 39), indicating CO and NO_x have also other sources than PM₁₀. This could be also due to the fact that the measurement van with the measurement instruments for NO_x and CO was located a certain distance from where the PM₁₀ was measured, and the van was at a road with a little traffic. The correlation between NO_x and CO is however found to be relative high with a correlation coefficient of 0.772 as shown in Figure 40. This indicates that most of these two gaseous pollutants are emitted from the same sources, which can be traffic or

residential oil firing or both. Since only very low CO comparing to NOx is emitted from oil firing (McDonald, 2009), which is also the dominant heating way in Dettenhausen, it is unlikely that residential oil firing is responsible for these two highly correlated compounds. Therefore, most of these measured NOx and CO can be only due to the traffic. This seems however to be contradictory to the discussion before in Chapter 4.3.3, where it is pointed out that the traffic is not an important emission source for NOx and CO and these are more likely to be emitted from biomass burning in this area. But since these values were measured under inversion weather conditions and remote pollutant transport can be excluded, it is reasonable to infer here that the little traffic did have a significant impact on the local pollutant concentrations in terms of NOx and CO during inversion periods as the emissions could not be dispersed.

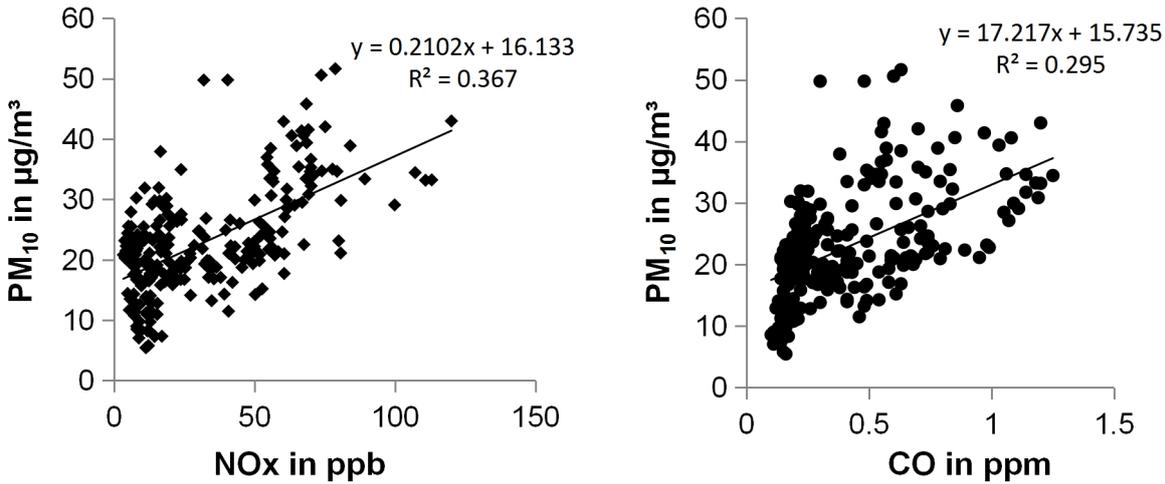


Figure 39: Correlation of outdoor PM₁₀ with NOx and CO

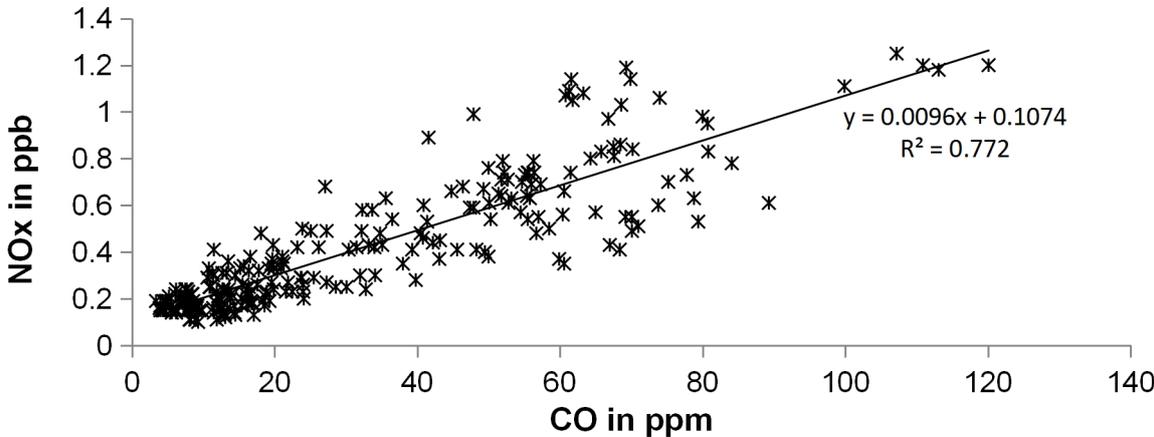


Figure 40: Correlation between NOx and CO (both instruments located in the van)

4.5.4.3 Comparison between indoor and outdoor PM₁₀ in terms of mass concentration

Indoor and outdoor PM concentrations were both measured with continuous and discontinuous techniques. Figure 41 shows the results from continuous measurements from midnight to 7 am on 11th February. As there were no indoor activities from 0:00 until 5:00 am, the PM₁₀ concentrations during this time period are considered to be indoor background concentrations. This average indoor background of 5 µg/m³ is noticeably lower and more stable than outdoor PM₁₀, which varies between 15 and 25 µg/m³ during this period. At 5:30 am, when the house owner got up and started wood firing, the indoor PM₁₀ concentration increases dramatically and reaches a peak of 55 µg/m³ at about 6:00 am. After half an hour, the concentration reduces to a level comparable to the outdoor concentration. This very sharp peak is due to opening of stove door for ignition and wood input. During the stable burning of wood, the PM₁₀ concentration inside the house decreases again to a relative low level, indicating no obvious leakage of particulate matter from the flue gas into the living room. Nevertheless, this concentration shows directly the contribution of wood burning to indoor PM₁₀.

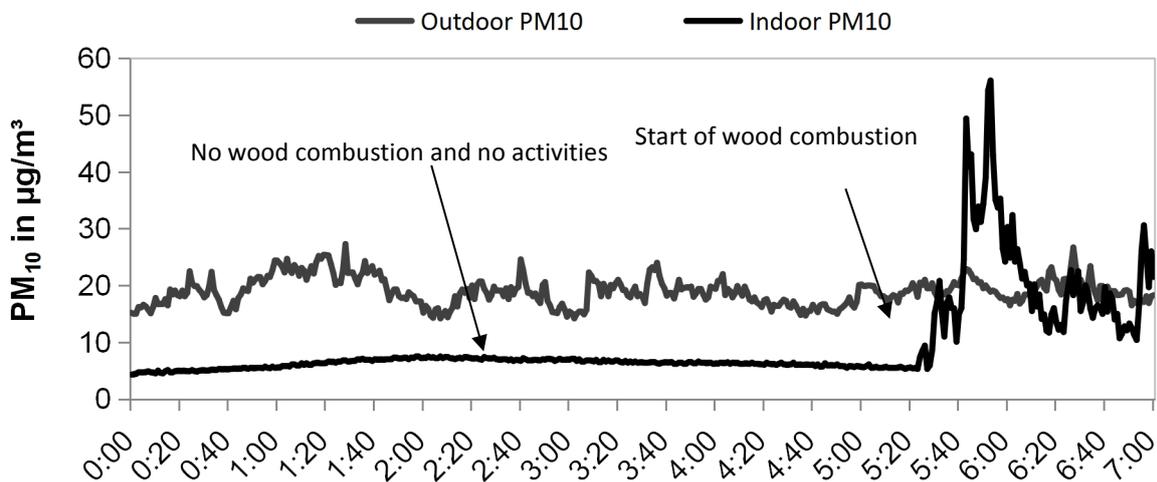


Figure 41: Continuous measurement of indoor and outdoor PM₁₀ on 11. February

Results from discontinuous measurement reflect the PM₁₀ pollution situation from another aspect as there is a significant difference in time resolution. In the collected four pairs of PM₁₀ samples, outdoor samples show comparable concentrations which are in the range

between 27 and 34 $\mu\text{g}/\text{m}^3$ and are much higher than those of indoor PM_{10} , with an average indoor to outdoor ratio (I/O) of 0.35 (Figure 42). This result reveals that under inversion weather conditions, the outdoor PM pollution has a remarkable level while daily average indoor PM_{10} concentration remains at a relative low level. Based on the results from continuous measurements, it is found that the indoor air quality was affected by wood burning due to ignition and refueling. This short term effect could, however, not be identified by discontinuous measurements as the opening of stove door happened only for a very short time and the sum of contribution is limited with regard to a long sampling duration up to 48 hours.

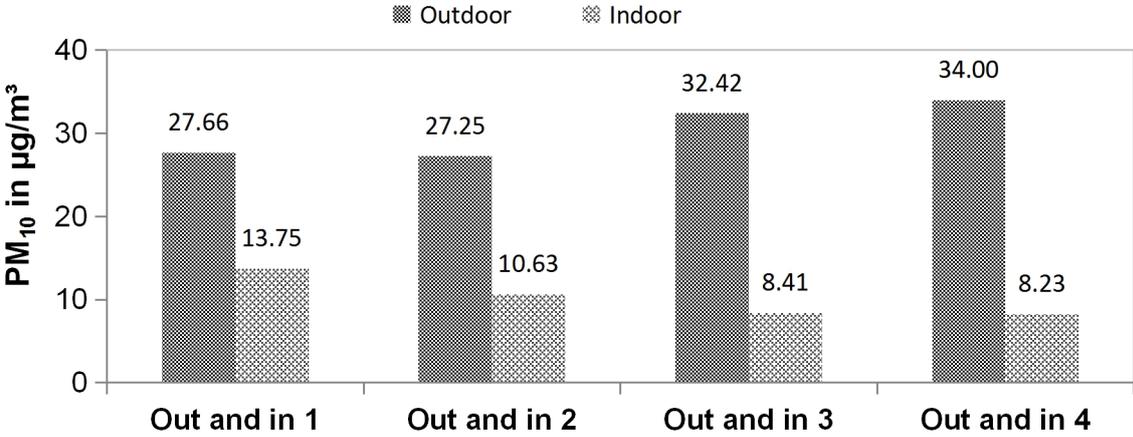


Figure 42: Comparison of indoor and outdoor PM_{10} measurement results (from two low volume samplers)

4.5.4.4 Comparison between indoor and outdoor levoglucosan

After determination of the PM concentration, the loaded filters were analyzed to determine their levoglucosan content as shown in Figure 43. The quantification of this chemical marker is to reveal the direct effect of biomass combustion to indoor PM. The results show that levoglucosan was detected in almost all samples except of one indoor sample. The reason for this can be due to the fact that an inversion weather condition during the sampling time for this sample was not very obvious and there were less heating activities (Figure 35). This can be also proved from the corresponding outdoor sample, which has also a relative low levoglucosan concentration. In general, outdoor levoglucosan levels are much higher

than that of indoor as expected, especially for the last two pairs when corresponding PM₁₀ also shows higher levels during lower night temperatures (Figure 35). Even with an obvious difference in the absolute concentration, the ratio of levoglucosan to PM₁₀ shows very comparable results for each pair. This indicates that both indoor and outdoor PM₁₀ could be mostly attributed to wood combustion emissions. The high values of the last two pairs show that wood combustion contribution to PM₁₀ is especially significant during inversion conditions. The smoke of these firings is locally concentrated because of the stable atmosphere during inversion.

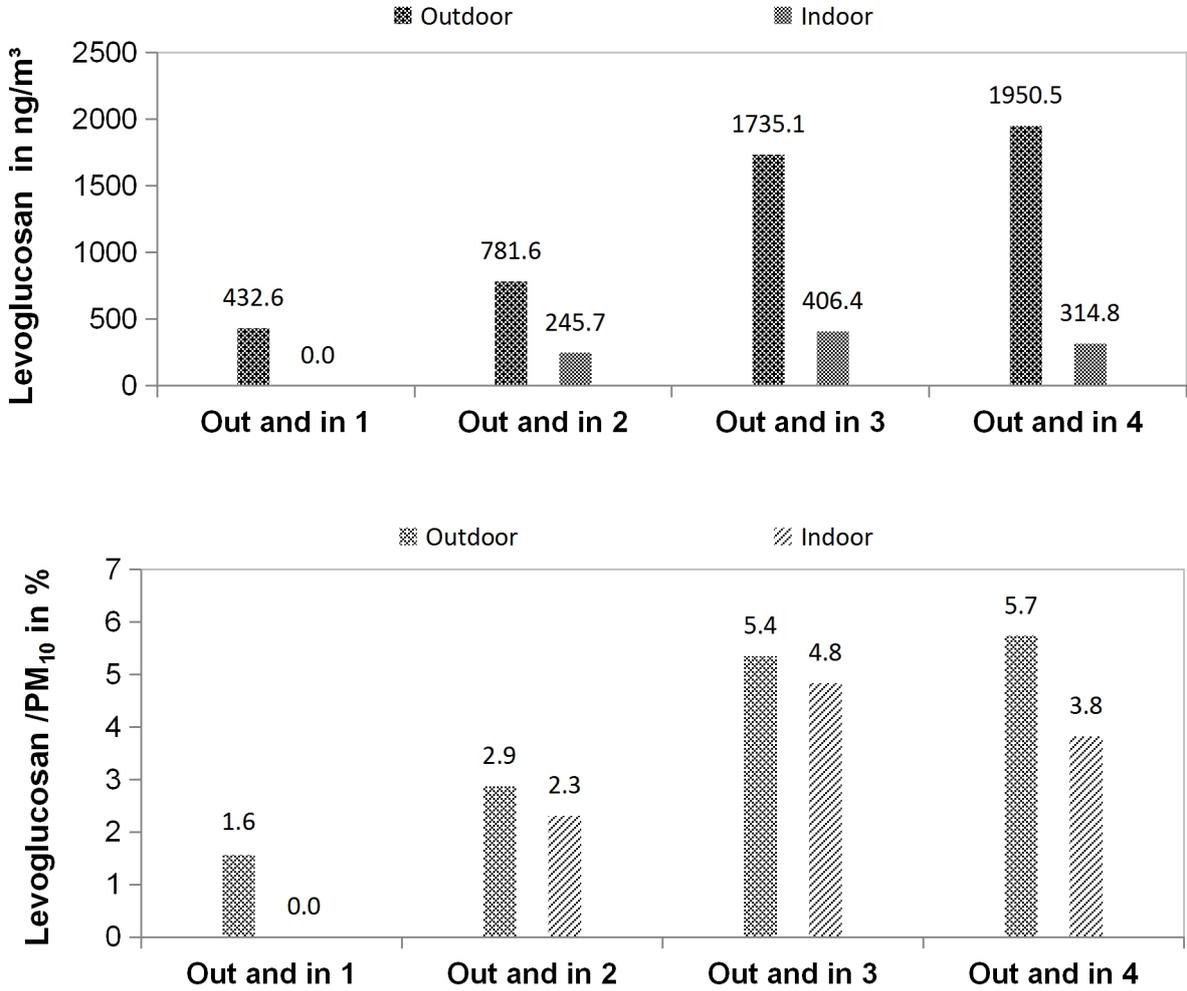


Figure 43: Comparison of indoor and outdoor levoglucosan (above: concentration, below: ratios of levoglucosan to PM₁₀)

4.5.5 Summary of the indoor air quality measurements

During a four-day measurement campaign, the indoor concentrations of wood burning pollutants in terms of PM₁₀, CO and BC were measured. It is found that devices for CO and BC measurements are relative sensitive and respond to each operation during wood burning activity by showing corresponding peaks, while some activities are not recognized with continuous PM₁₀ monitoring. Except these peaks, indoor concentrations of these pollutants are found to be relatively low. That means, the indoor air quality shows some very short time effects with wood burning activity in house, mainly during the opening of the stove door. By comparing indoor and outdoor PM₁₀, contribution of wood combustion to indoor PM is very low and cannot be identified with discontinuous measurements. Average daily concentrations of indoor PM₁₀ and its levoglucosan contents are much lower compared to their outdoor levels, implying the refreshing of indoor air by opening windows during inversion periods should be with caution since the indoor air quality could be affected by the penetration of higher outdoor PM.

To summarize, indoor air quality was only slightly and shortly affected by wood burning due to opening of the stove door. After a short period, indoor pollutant concentrations remained stable and at quite low levels. Possible exposure to indoor wood smoke pollution happened mostly during ignition and fuel replenishment, while the outdoor PM concentrations were always higher.

4.6 Summary and conclusions of the winter measurements

During the ambient air measurements and a short-term case study for indoor air pollutants, the local air pollution was recognized through the concentration determination of various pollutants.

During winter 2013/2014 and winter 2014/2015, PM₁₀ level remained below the EU limit value with only one sample exceeding 50 µg/m³. The average concentrations for two winters were both approximately 20 µg/m³, despite of the fact that several inversion periods happened during the measurement periods and corresponding higher daily average PM₁₀

concentrations were observed. This also proved the negative influence of inversion conditions on the pollutant dispersion. PM-bound total PAHs and BaP presented the same trends in temporal courses and were strongly correlated to each other. Daily average of BaP exceeded 1 ng/m^3 very often and the carcinogenic PAHs had a contribution of 65 % to the total PAHs, indicating potential health risks for local people due to air pollution.

Black carbon (BC) was measured the first time in this residential area and the results show that the BC concentration is as high as 5000 ng/m^3 , with the most frequent concentrations between 1000 and 3000 ng/m^3 . The high peaks observed correspond to high PM_{10} concentrations during an inversion period in February 2015. The average diurnal trend shows peaks from morning and evening BC which could be explained by the combined contribution from wood burning and oil firing for residential heating. Relative good correlations are observed between BC and gaseous pollutants (NO_x and CO). The specific contribution from wood burning is defined as biomass burning black carbon (BB BC) and data are directly delivered from the Aethalometer AE33 measurements. Biomass burning BC is found to be nearly half of the corresponding total BC, accounting for a contribution between 17.8 and 61.7 % to total BC.

The wood burning tracer levoglucosan was detected in all ambient PM samples, with an average concentration of about 335 ng/m^3 . Good correlations between levoglucosan and other pollutants (BaP, BC, OC and EC) suggested that residential wood burning was an important emission source for these pollutants in this area. The ratios between levoglucosan and PM_{10} show different patterns for two winters. In winter 2013/2014, ratios remained relative stable within a small range between $0.006 - 0.031 \text{ } \mu\text{g}/\mu\text{g}$, while the ratios in winter 2014/2015 showed significant variations, with some peaks as high as $0.13 \text{ } \mu\text{g}/\mu\text{g}$. The high peaks were mainly correlated to heating intensities of residents, which depended further on weather conditions. Meanwhile, the fluctuations of the ratios indicated that PM_{10} might have other emission sources besides residential wood burning. Within all these possible emissions sources, PM_{10} emitted from residential wood burning could not be identified or quantified directly from the collected ambient PM_{10} samples. The fraction of PM_{10} stemming from

wood burning and found in the total ambient PM₁₀ samples is defined as wood burning contribution to ambient air PM₁₀, which is possible to be quantified by using levoglucosan as wood burning tracer with a substantial input of levoglucosan in ambient air in this area. The quantification of this parameter is the so-called source apportionment. According to the calculation principle and procedure stated in Chapter 2.3.2, besides the ratios of levoglucosan to PM₁₀ measured from ambient samples, the emission ratios of levoglucosan at an emission source need to be determined for the calculation.

The influence of firing an indoor chimney stove on the indoor air quality was studied through measurements of various air pollutants. The results show that indoor concentrations of PM₁₀, CO and BC increased slightly during ignition and fuel replenishment, which proved some exposure to indoor wood smoke. The contribution of these operations on a daily average concentration of PM₁₀ was, however, very low. Therefore, the influence from wood combustion on indoor air quality is limited when the wood stove is appropriately installed and no leakage of flue gas happens. A comparison with outdoor PM₁₀ suggested that under inversion weather, the outdoor PM pollution was distinctly higher than the indoor concentrations and had a greater influence on the indoor air quality, e.g., by opening windows, than the operation of an indoor chimney stove in the room.

To summarize, the ambient air in the studied area is affected by residential wood combustion smoke to a certain extent and the pollution is serious under inversion weather conditions. The local air quality could be significantly improved through the reduction of wood combustion smoke for room heating by using optimized technologies and operation conditions. For a better indoor air quality, emission sources should be also controlled by a careful opening of the stove door as short as possible. Opening of windows and doors for ventilation should be also paid attention to under inversion conditions with high ambient PM concentrations in order to avoid penetrating of outdoor PM. In order to quantify the wood burning contribution to total ambient PM₁₀, investigation of levoglucosan emission ratios at emission sources is necessary and corresponding investigations are discussed in Chapter 5.

5. Levoglucosan sampling process and emission behavior at an emission source

As levoglucosan is considered as a unique wood burning tracer, its significant concentration measured from ambient PM₁₀ in the investigated residential area (as discussed in Chapter 4) indicates clearly that the air is polluted by residential wood burning smoke in this area during winter periods. In order to quantify the share of PM from wood burning in ambient PM by using levoglucosan as tracer, the next task is to determine the emission ratio of levoglucosan/PM directly from flue gas at an emission source. With regard to the situation of small combustion systems in Germany or even in Europe, wood stoves are the dominant appliances in private households. Therefore, the emission source is here referred to wood burning in a wood stove.

5.1 Experimental method, design and procedure

With regards to the motivation stated in Chapter 3.1.3 and 3.1.4, sampling of levoglucosan could be carried out directly at the flue gas from a wood stove, aiming to at first investigate the sampling process and then to find out the emission characteristics of levoglucosan. Based on the objectives and literature review, the corresponding experiment is defined as "combustion experiment" and was carried out in locally used wood stoves with locally used wood types. Therefore, a log wood stove was selected as the small combustion unit and a dilution tunnel was designed and built up to simulate the sampling of PM behind the chimney. Several experimental parameters have been taken into account for the design of the experiment structure, for example, operation conditions and sampling techniques. Details of each experiment design are discussed in the corresponding sections below.

5.1.1 Built-up of a dilution tunnel and experimental set-up

A dilution tunnel was designed with reference to the EPA method 5G (US Environmental Protection Agency 2000) and NS 3058-2 (1994) and constructed inside the technical plant of

the Institute of Combustion and Power Plant Technology (Figure 44 and Figure 45). The tunnel is approximately 5 meter high to the ground. A fan is connected at the end of the tunnel and its performance can be regulated through the adjustment of frequency. The expected function of this dilution tunnel system is to capture all the flue gas emitted from the connected combustion unit, to dilute the full-flow of hot flue gas using ambient air as dilution gas and to cool it down to nearly ambient conditions. The structure of the whole experimental setup is depicted in the sketch in Figure 44.

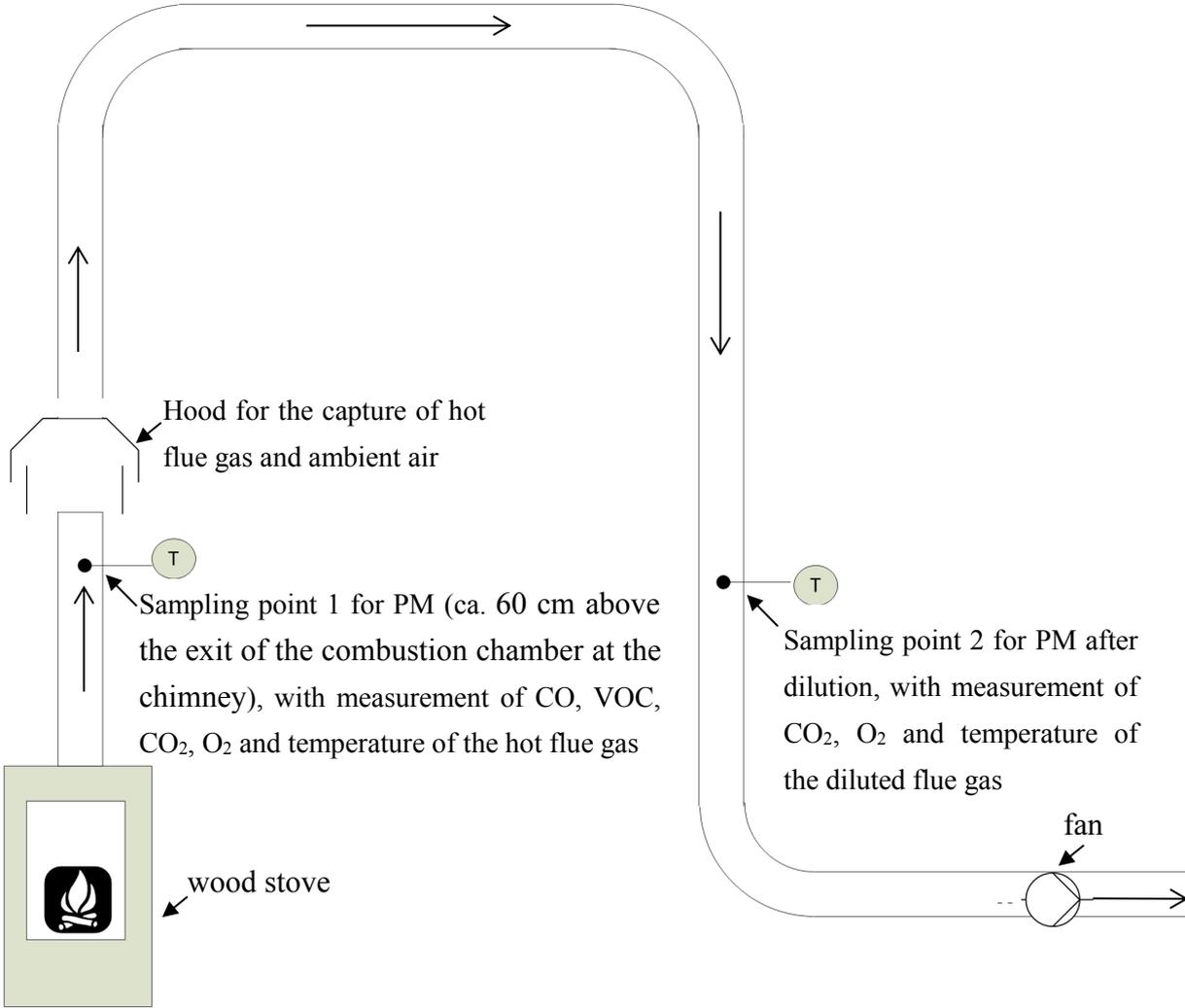


Figure 44: Sketch of the experimental setup for levoglucosan sampling at a wood stove



(a)



(b)

Figure 45: Dilution tunnel connected with a log wood stove and measurement techniques (a) and wood stove used for the combustion experiments (b)

The function of the dilution tunnel is tested through draft determination (US Environmental Protection Agency, 2000), which is realized through the adjustment of the distance between the hood and chimney together with the regulation of the fan performance for a suitable draft. During the wood firing, the emitted smoke was captured completely from the hood even under maximal burning rate, which indicated the draft was suitable for the experiment (US Environmental Protection Agency, 2000). Ambient air is drawn through the hood as dilution air without pre-treatment, the flow rate of which is controlled by the frequency of the fan. The tunnel serves as the route for hot flue gas to mix with the ambient air. The hot flue gas is cooled down to a certain temperature range at the end of the tunnel, where PM samples are collected (Figure 44).

The dilution ratio is defined as the ratio of total flow volume (at sampling point 2) to the volume of undiluted hot flue gas at sampling point 1, which is calculated by the CO₂ content ratio before and after dilution. Before testing the dilution ratio, the two CO₂ measurement instruments were tested to make sure they have the same responses. After each measurement campaign, they were regularly controlled and adjusted to ensure stable performance during the measurement period. It is found that the range of dilution ratios could be regulated

between around 4 and 10 by adjustment of the fan and depended solely on its performance, which is an important setting for the future experiments.

5.1.2 Experiment program

A commercial available log wood stove (Hase-MODENA, 8kW) was applied as combustion appliance for the experiments with two commonly used wood types in Dettenhausen, which are beech wood (hardwood) and spruce (softwood). According to the study objectives, continuous sampling before and behind dilution and combustion phases sampling were designed and applied for PM-bound levoglucosan. Combustion phases sampling is referred to collecting samples from different combustion phases within each combustion cycle, while "continuous sampling" here means a sampling process non-stop for 15 minutes, covering all the combustion phases. The experiment categories are named after these methods (Table 10).

Table 10: Categories of combustion experiments with a log wood stove

Combustion system	A commercial available log wood stove (Hase - MODENA, 8kW), primary air and secondary air could be regulated through opening	
Fuel	Wood type	Water content (%)
	Beech wood (hardwood)	13.8 - 15.3
	Spruce (softwood)	10 - 11
Experiment design	Objectives	
Continuous sampling before and behind dilution	To compare the emission levels before and behind dilution during the first 15 minutes of the combustion process	Development of a suitable sampling procedure for levoglucosan with the dilution technique and determination of emission ratios of levoglucosan
Combustion phases sampling	To investigate the emission of PM-bound levoglucosan from three combustion phases	

The experiment variables are the operation, combustion and sampling conditions (Table 11). The operation conditions include "Fuel load" and "Start mode". "Fuel load" is referred to the wood amount for each combustion cycle, which corresponds to different thermal output.

"Start mode" is referred to the status of the wood stove when the combustion starts, including 'hot start' and 'cold start'. Cold start represents the first combustion cycle on each measurement day, before which the combustion chamber reaches ambient temperature. "Combustion conditions" are separated into good combustion and normal combustion based on different airflow settings in terms of both primary air and secondary air, which could be regulated through adjustable air inlets. Restrict and enlarge the airflow are expected to slow and accelerate the combustion process, respectively. The ignition is referred to the phase starting from igniting to the appearance of flame. The dilution ratio setting is assigned as one of the sampling conditions.

Table 11: Definition of operation, combustion and sampling conditions

Operation condition	Fuel load	partial load	full load		
		1.1-1.3 and 1.5 kg	2 kg		
	Start mode	cold start and hot start			
Combustion condition (airflow setting)		Ignition	Good combustion	Normal combustion	
	Primary air	complete open (100 %)	1/2 open (50 %)	complete closed (0 %)	
	Secondary air	complete open (100 %)	1/2 open (50 %)		
Sampling condition		Continuous sampling before and behind dilution	Combustion phases sampling (behind dilution)		
	Dilution ratio	8	5, 8 and 10		
	Sampling start point of each phase	Appearance of visible flame after ignition	CO₂ content in hot flue gas (Vol.-%)		
			Burn-up: ca. 3 %		
			Main-burning: ca. 10 %		
			Burn-out: ca. 5 %		
	Sampling duration	15 minutes	The first 3, 6 and 6 minutes for each phase, respectively		
Sampling positions	Sampling point 1: direct at the chimney, about 60 cm above the exit of the combustion chamber				
	Sampling point 2: at the end of the dilution tunnel				

Based on the specific objectives, the experiment design for two sampling methods was carried out by combining the listed variables, which are defined as experiment conditions. Continuous sampling before and behind dilution was carried out firstly to prove the application of the dilution tunnel and in the second step to investigate the possible influence of combustion and operation conditions on the emission level of PM. The corresponding measurement program is shown in Table 12 in terms of dilution ratio, fuel application and combustion conditions.

Table 12: Experiment program for continuous sampling before and behind dilution

Wood type	Combustion condition (airflow setting)	Dilution ratio	Start mode	Fuel load
hardwood	good combustion	8	cold and hot start	partial load
	normal combustion		cold and hot start	full load
softwood	good combustion		cold and hot start	partial load
	normal combustion		hot start	

The experiment plan for combustion phases sampling was similar to this but with two more dilution ratios for the sampling process. Specific experiment settings for each campaign are presented in the corresponding results sections.

5.1.3 Sampling technique and measurement procedure

The specific experiment tasks include sampling of particulate matter-bound levoglucosan, and simultaneous continuous online-measurement of gaseous compounds and temperature in the flue gas at the two measurement points (Figure 44). In emission studies, total PM is normally measured and compared to PM₁₀ in ambient air, since previous studies have shown that up to 90 % of the total fine particles emitted from wood burning is PM₁₀ (Baumbach et al., 1999). Total PM was sampled from the wood combustion experiments in this study. The PM sampling procedure followed the standard VDI 2066-part 1 (2006). Experiment program has covered different combined settings as shown in Table 12, but the general procedure is similar and is described briefly below, which includes mainly three parts: preparation, firing process, and PM sampling together with on-line measurement.

Prior to each measurement campaign, preparations for filters, wood and measurement devices were carried out according to corresponding protocols. Firstly new quartz fiber filters (47mm, MK, Germany) were conditioned and weighted as specified in DIN EN 12341 (2014). In the technical plant, wood was cut and weighed for each batch and the ash in the wood stove from the previous day was removed. The applied instruments for the gaseous flue gas compounds and relevant parameters together with measurement principles are listed in Table 13. These measurement instruments were controlled and adjusted before and after each campaign. The sensors and the PM sampling train were connected to the chimney or dilution tunnel.

Table 13: Measurement techniques for gaseous species in flue gas

Parameter	Measurement principle	Measurement device	Measurement range	Concentration of calibration gas
CO ₂ [Vol.-%]	non-dispersive infrared	NGA 2000	0-20	12.1
CO [ppm]	non-dispersive infrared	NGA 2000	0-1500	802
CO [Vol.-%]	non-dispersive infrared	NGA 2000	0-3	0.701
O ₂ [Vol.-%]	paramagnetic	NGA 2000	0-25	10.2
VOC [ppm]	flame ionization	FID TESTA	0-1000 and 0-10000	804

After carrying out all preparation steps, the firing process started with using a small amount of wood (500 g to 800 g) for ignition. This process lasted for a few minutes and then 2 to 3 pieces of wood, which weighed from 1.1 to 2.0 kg depending on the specific experiment design, were put into the combustion chamber and the stove door was immediately closed. The flue gas from the combustion chamber was emitted into the chimney exhaust pipe and then went into the dilution tunnel via the hood .

The measurement program for temperature and gas compounds of the flue gas was controlled by computer and started before ignition. After wood input, the PM sampling was started when a visible flame was observed, meanwhile primary air and secondary air were manually adjusted according to the specific experiment design. The sampling and

measurements mainly took place at two measurement points (Figure 44). Isokinetic sampling of PM was performed with flue gas being withdrawn from the center of the cross-section of the chimney using conventional dust sampling equipment with reference to VDI 2066 part 1 (2006) and VDI 4206 part 2 (2011) (Figure 46). Compositions of flue gas are characterized in terms of carbon monoxide (CO), carbon dioxide (CO₂), oxygen (O₂) and volatile organic carbon (VOC), which deliver information about the combustion quality. The second sampling point is at the downstream of the dilution tunnel where the flue gas is already diluted with ambient air which came through the hood (Figure 44). CO₂ and O₂ are also measured at this point for the calculation of the dilution ratio. The flue gas velocity is determined using a vane anemometer near the second sampling point. The residence time for flue gas inside the dilution tunnel is estimated to be between 1.2 and 2.6 s based on the length of dilution tunnel and flue gas velocity (3 to 6.5 m/s). The temperatures are measured inside the combustion chamber besides the two sampling points.

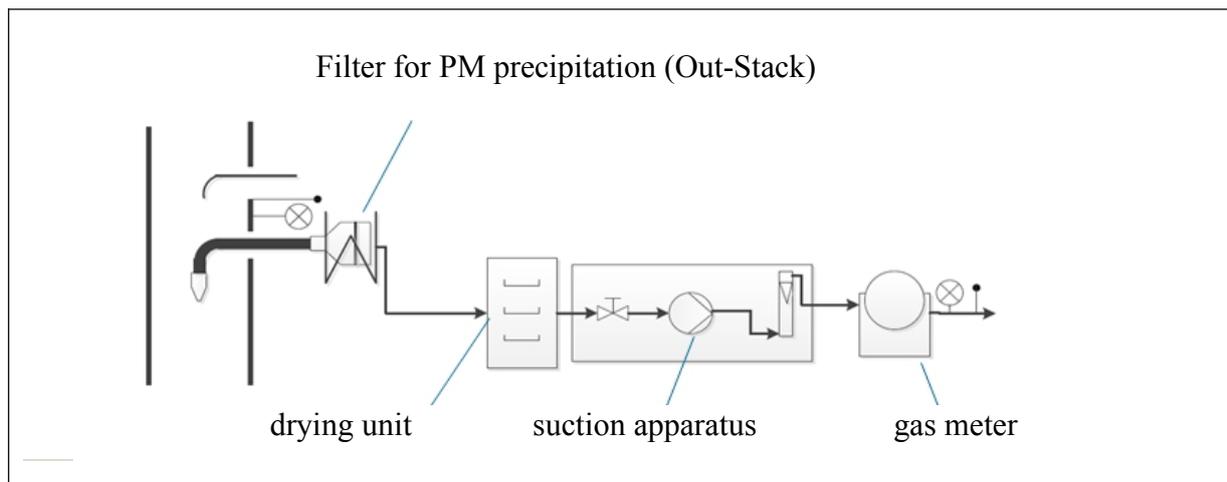


Figure 46: Sampling line of PM according to the reference measurement procedure for measurements at small combustion units according to VDI 2066 part 1 (2006) and VDI 4206 part 2 (2011) (adopted from Schäfer, 2016, p. 36)

After each measurement campaign, the on-line data of the flue gas components were processed for a control of the experiment quality. Some experiments were repeated in the next campaign if necessary. The collected PM samples were conditioned and weighed for the calculation of the PM mass concentration according to VDI 2066 part 1 (2006).

5.2 Results of continuous sampling before and behind dilution

Sampling of PM-bound levoglucosan simultaneously at the two measurement points (see Figure 44) is defined as continuous sampling before and behind dilution since PM samples are collected from both hot flue gas and diluted flue gas, which are at 0.6 m above the exit of the combustion chamber and at the end of the dilution tunnel, respectively. The initial motivation is to investigate the dilution effect by comparing emission levels before and after dilution.

Different operation conditions are set for sampling experiments in terms of airflow setting and fuel load. The airflow setting is realized by the opening of air inlets for both primary air and secondary air, which are adjusted to be completely closed or half open, presented by 0 and 50 %, respectively. According to this, combustion conditions are defined as "normal combustion" and "good combustion" (Table 11). Experiments were performed with partial load and full load, covering both a cold and a hot start according to the experiment program in Table 12.

5.2.1 Characterization of combustion parameters

By using the sampling procedure described in Chapter 5.1.1, PM samples were taken for 15 minutes after ignition for each combustion cycle. Depiction of combustion products in terms of VOC, CO and CO₂, O₂ and temperatures of hot flue gas from a combustion process is shown in Figure 47. The whole process lasts for one and a half hour and includes two complete burning cycles. The highlighted area represents the operation of wood input, where CO and VOC show high peaks after ignition. Sampling start point and duration are also shown.

The combustion quality is characterized in terms of these mentioned parameters, which correlate strongly to the combustion temperature. In this study, the combustion temperature is measured as the temperature inside the combustion chamber, which can also be presented by the temperature of the hot flue gas. Both cycles began with high emission levels of CO and VOC, corresponding to relative low CO₂. When the process entered into a stable

combustion, high CO₂ and hot flue gas temperatures are observed while O₂, CO and VOC dropped dramatically. VOC is about one tenth of CO over the whole combustion process. These are typical evolution patterns, indicating a normal combustion process and a stable performance of the measurement instruments during the experiments.

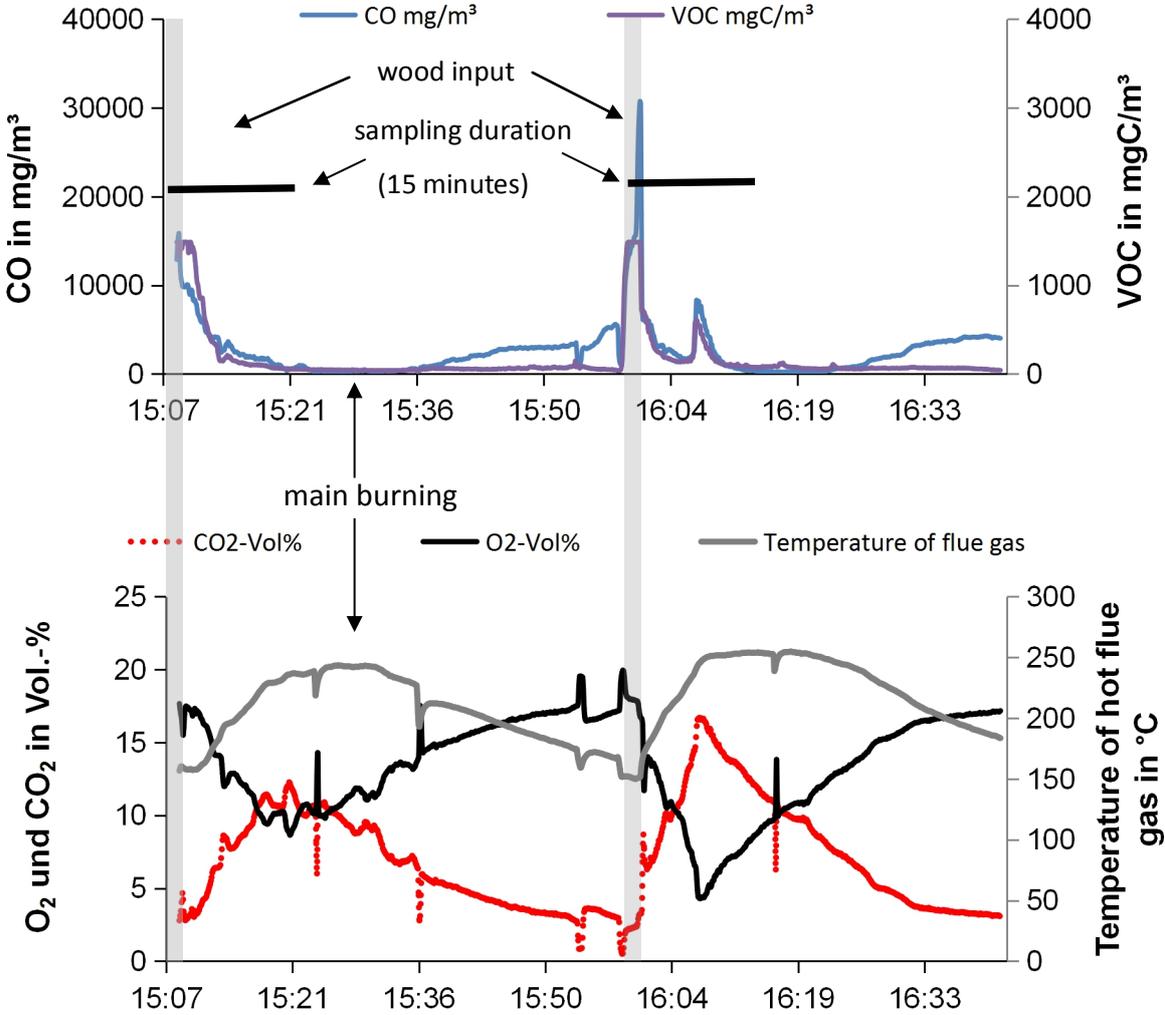


Figure 47: Depiction of hot flue gas compositions and temperature in two consecutive combustion cycles: CO and VOC profiles (above) , CO₂, O₂ and hot flue gas temperature profiles (below)

5.2.2 Combined effects of dilution and condensation

Based on performed valid combustion cycles, emission levels in the hot flue gas and after the dilution tunnel in terms of PM and levoglucosan are attained. The emission levels measured at the dilution tunnel are actually the results of combined effects from dilution and

possible condensation of semi-volatile compounds including levoglucosan on PM (formation of new PM) during the cool down process.

Therefore, for an evaluation of the condensation effect, the influence from dilution is first eliminated by multiplying the concentrations measured at the dilution tunnel with the corresponding dilution ratios. In this way, the combined effects of dilution and condensation or new PM formation processes are separated. The recalculated concentrations of PM and levoglucosan are only correlated with condensation or formation.

In terms of PM and levoglucosan, the ratios of recalculated values to undiluted values are compared under partial load and full load conditions and the results are shown in Table 14.

With regard to PM, if there is no condensation of semi-volatile compounds and no formation of new PM, the concentration of PM behind dilution $(PM)_{beh}$ and PM before dilution $(PM)_{bef}$ from the same experiment should be the same, as PM behind dilution is the original PM already exiting in hot flue gas. Since the ratios listed in Table 14 are all > 1 , these prove that there is always a formation of new PM during the dilution. This agrees well with the results from some previous studies (Struschka, 2001). It seems that the results in the partial load case present a more significant contribution of fresh PM after dilution for cold-start compared to hot-start. However, these values are relative comparable within two load conditions in comparison to those of levoglucosan.

The ratios of levoglucosan behind dilution $(Levo)_{beh}$ to levoglucosan before dilution $(Levo)_{bef}$ show significant higher values in full load operation than corresponding tests with partial load. It seems that a large amount of levoglucosan is in the gas phase in the hot flue gas and emitted as incomplete combustion product under full load condition. It is also observed that ratios under normal combustion are higher than those under good condition. For a better understanding, the amount of levoglucosan measured from both before and behind dilution is shown with corresponding combustion temperature and flue gas temperature in Figure 48.

Table 14: PM and levoglucosan ratios between diluted flue gas (at the end of the dilution tunnel, behind dilution \times dilution ratio 8) and hot flue gas (at the chimney, before dilution)

Conditions		Full load (2 kg)		Part load (1.2 - 1.5 kg)	
		$(PM)_{beh} / (PM)_{bef}$	$(Levo)_{beh} / (Levo)_{bef}$	$(PM)_{beh} / (PM)_{bef}$	$(Levo)_{beh} / (Levo)_{bef}$
Normal combustion	cold	2.1	46.9	3.1	4.3
	hot	2.2	52.8	1.6	8.4
Good combustion	cold	1.6	11.7	5.2	3.9
	hot	1.3	22.4	1.0	1.5

It can be seen in Figure 48 that the hot flue gas temperatures are all below 300 °C. With regard to the condensation temperature of levoglucosan, which is about 380 °C, it can be inferred that there is levoglucosan condensation on PM in the hot flue gas. However, the amount of levoglucosan measured in the hot flue gas is much lower than that measured behind the dilution for all the combustion cycles, especially under full load combustion, which results in the very high ratios in Table 14. This result proves the function of the applied dilution tunnel, which simulates the cool down and dilution process of hot flue gas when it emits into the ambient air. The small amounts of levoglucosan under full load conditions can be explained by the corresponding high combustion temperatures, which are obviously higher than those under partial load combustion (see Figure 48).

It is also observed from Figure 48 that levoglucosan with cold start generally shows higher concentrations than those with hot start independent of the airflow conditions, which correspond to also relative lower combustion temperature compared to hot-start cycles especially under good combustion. But no obvious trends can be observed by the comparison of the results between full load and partial load under the same combustion condition (airflow setting).

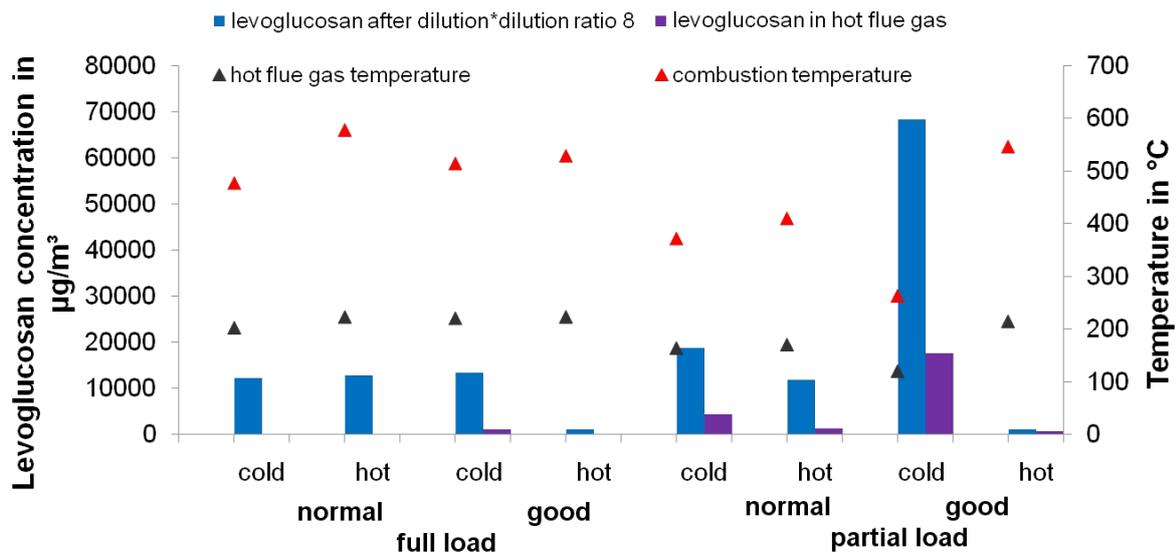


Figure 48: Partial load and full load: levoglucosan amount behind and before dilution with corresponding combustion temperature and hot flue gas temperature under different operation conditions (hardwood, dilution ratio: 8)

To summarize, the ratios of PM at two sampling points show that there is always formation of new PM during dilution with cooling, but no significant difference is found under the given airflow settings and fuel load conditions. The ratios of levoglucosan are significantly higher under full load operation. The measured concentrations of levoglucosan show a strong correlation to the kind of start mode, since a higher emission of levoglucosan is found under cold-start cycles independent of airflow setting and fuel load but correspond to the lower combustion temperature. Influence of operation conditions (airflow setting and fuel load) on the measured levoglucosan level is not obvious within these performed experiments. This agrees with the findings from Engling et al. (2006).

These results show that it is necessary to use a dilution tunnel for levoglucosan sampling and the levoglucosan level has to be measured after the dilution instead of that from hot flue gas to get a figure of the realistic emission ratios for further source apportionment studies. Therefore, further levoglucosan samplings were all carried out behind dilution.

5.3 Emission behavior of levoglucosan from three combustion phases

In Chapter 5.2, the influence of combustion and operation conditions on the levoglucosan emission level measured behind dilution is investigated. The experiments of combustion phases sampling in this chapter are designed to investigate the evolution process of levoglucosan during different combustion phases with different dilution ratios. Combustion phases are defined as **burn-up**, **main-burning** and **burn-out**. The division of these three phases is based on the CO₂ content in undiluted hot flue gas as shown in Table 11. The sampling durations for these three phases are the first 3, 6 and 6 minutes of each phase, respectively. That is, sampling for the burn-up phase begins on flame appearance when CO₂ is about 3 Vol.-%. After the burn-up phase, the starting point of main-burning is defined as CO₂ content reaches to about 10 Vol.-%. The sampling of the burn-out phase starts when CO₂ decreases to about 5 Vol.-%. Each phase lasts longer than each sampling duration (Figure 49).

The corresponding experiment plan is similar to that shown in Table 12 in Chapter 5.1. Briefly, sampling experiments for hardwood are carried out using three dilution ratios under both good and normal combustion. The fuel input is between 1.1 and 1.3 kg for each combustion process. More parameters are investigated with a dilution ratio of 8, for example, full load with 2 kg. Softwood is also investigated for certain combustion cycles with a dilution ratio of 8. In total 13 combustion tests were conducted for combustion phases sampling (10 for hard wood and 3 for soft wood) and 33 filter samples were collected.

5.3.1 Characterization of the combustion process

Combustion experiments of hardwood in the wood stove were carried out according to the process described in Chapter 5.1.3 with online measurement of hot flue gas compositions and temperature. Similar to the combustion process from sampling before dilution and behind dilution, the temperature, VOC, CO and CO₂ measured from the hot flue gas during

one combustion cycle are presented together with the temperature inside the combustion chamber in Figure 49.

It is obvious that CO and VOC show similar courses in the burn-up phase and in the part of main-burning phase, but VOC emission is about one tenth of CO, which indicates stable experimental conditions as expected. Very clear different phases can be observed directly from the combustion cycle in terms of these combustion products. At the beginning of combustion, CO and VOC are emitted at high levels as incomplete combustion products after ignition. When the burn-up combustion phase enters into the main-burning, these levels decrease dramatically. At the end of the main-burning, CO increases again slightly until the end of the burn-out phase, during which both the temperature of the hot flue gas and the temperature inside the combustion chamber decrease to below 200 °C. This CO₂ course is very important because it is used as the determinant factor for the phase division. It is observed that the concentration evolution of CO₂ agrees with the definition in each phase as stated in Table 11. As one of the complete combustion products, CO₂ shows a very similar course to those from both the temperature inside the combustion chamber and the temperature of the hot flue gas, but presents an inversed trend to CO through the whole process. In total 11 combustion cycles were selected as valid experiments for the investigation of levoglucosan and other parameters.

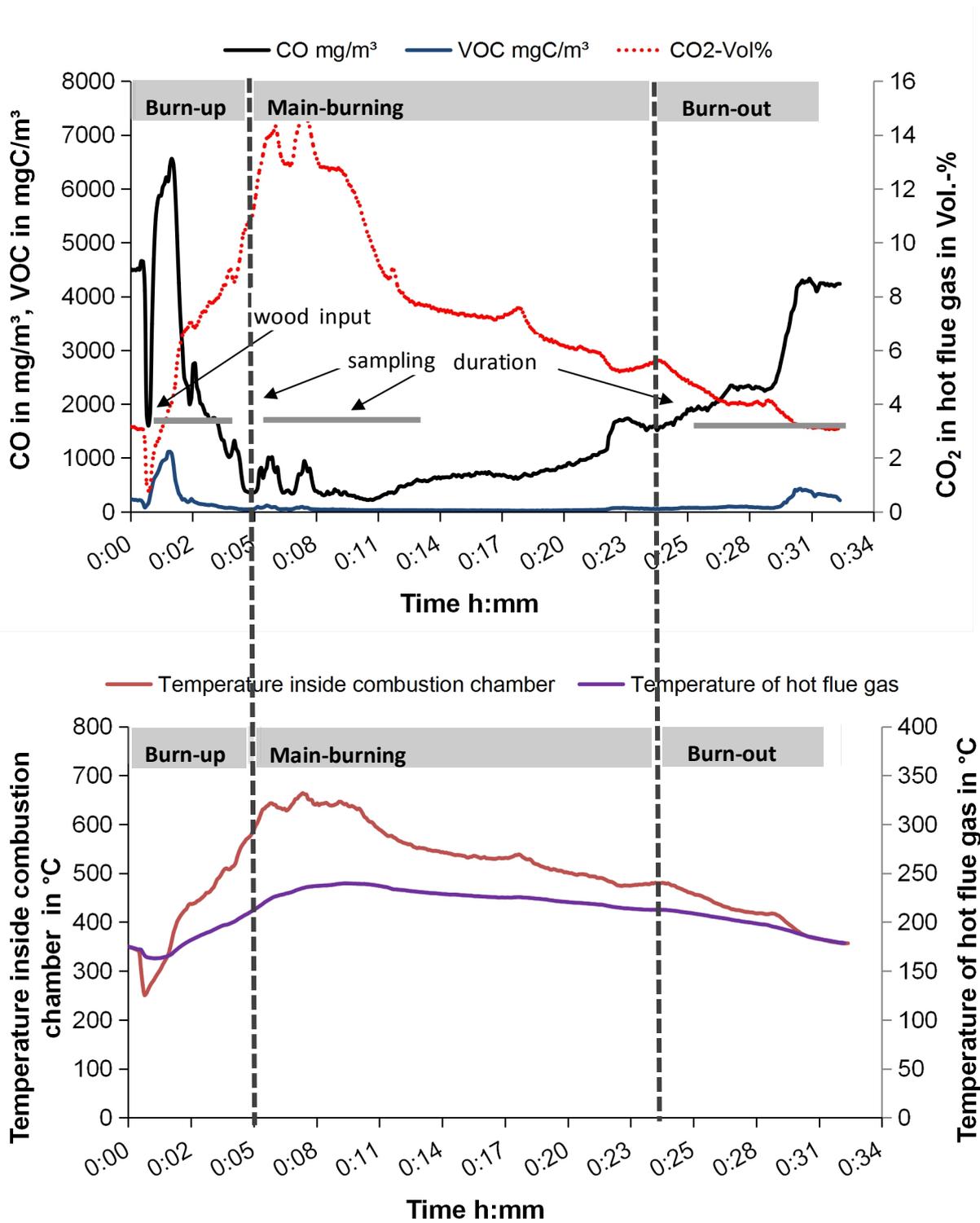


Figure 49: On-line measurements of CO, VOC and CO₂ in hot flue gas (above) and temperatures of the hot flue gas and inside the combustion chamber (below) under good combustion condition (hardwood, partial load, time resolution: 5 s)

Correlations between CO and VOC for the three combustion phases are presented separately in Figure 50. The results show a coefficient of 0.448 for the burn-up phase and a coefficient of 0.492 for the burn-out phase, while the main-burning has a much better correlation ($R^2 = 0.868$), which could be due to a stable combustion during this phase. These relative good correlations indicate a stable and reliable performance of the measurement techniques during the experiments.

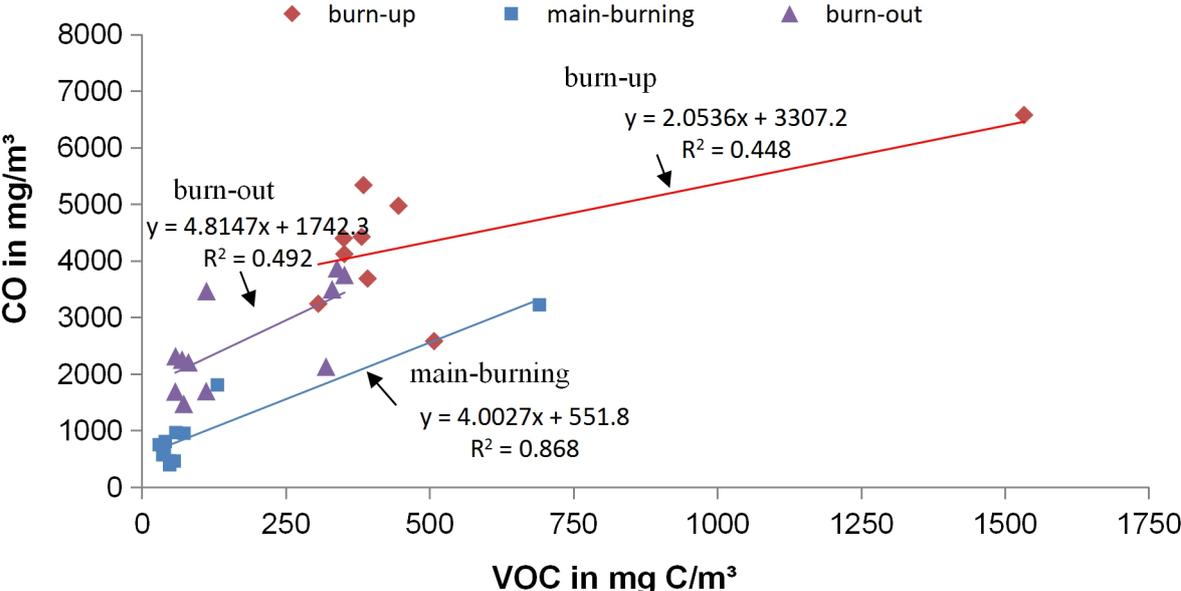


Figure 50: Correlation between CO and VOC for 11 combustion cycles (hard wood and softwood)

Average values of temperature inside the combustion chamber at three phases are presented in Figure 51. A typical pattern during each combustion cycle can be observed. First, the temperature at the burn-up phase is relative low but reaches quickly the highest values in the main-burning phase, and then decreases during the burn-out phase. Values from hardwood combustion cycles are slightly higher than those from softwood. Similar trends are observed for the temperatures of hot flue gas, which are all below the condensation temperature of levoglucosan. But the differences between two wood types become smaller when taking into account the standard deviations from hardwood combustion. A standard deviation for softwood combustion makes not much sense since there are only three combustion cycles.

Nevertheless, the corresponding results for hardwood and softwood are discussed separately in Chapter 5.3.2 and Chapter 5.3.3, respectively, with the main focus on hardwood. This approach makes sense since it is based on the fact that mainly hardwood is burned in the investigated residential area.

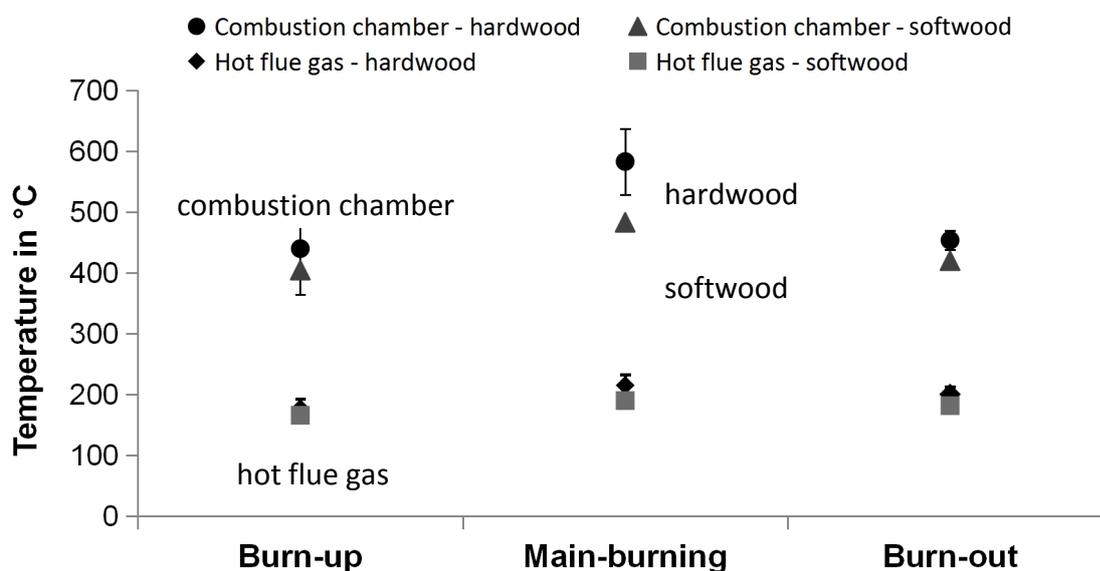


Figure 51: Average values and standard deviations of the temperature measured inside the combustion chamber and the temperature of hot flue gas at three combustion phases for both hardwood and softwood (11 combustion cycles: 8 for hardwood and 3 for softwood)

5.3.2 Results of hardwood combustion

Results from the three combustion phases of the 8 valid combustion cycles for hardwood are shown in Figure 52 in terms of PM concentrations (above), levoglucosan and VOC (middle) and corresponding temperatures (below). The highlighted cycles are combustion cycles with cold start.

It is first observed that PM shows different concentrations at different combustion phases, and concentrations at burn-up phases are general higher than those from the other two phases. The trend is also observed for levoglucosan, which is found in all PM samples. Therefore, higher levoglucosan corresponds to higher PM. The potential influencing factors on levoglucosan level are discussed below in terms of combustion temperature and start mode based on the observation of Figure 52.

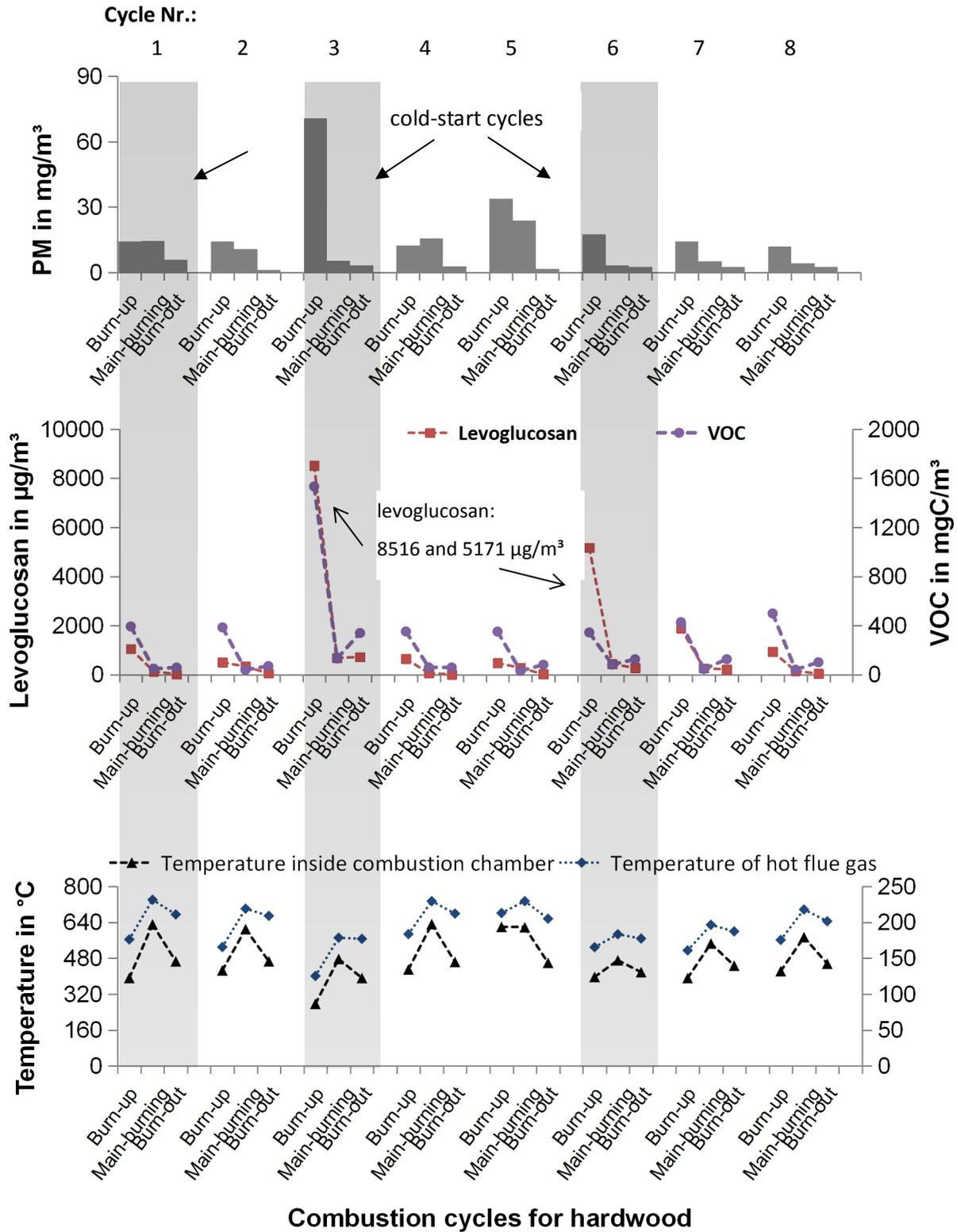


Figure 52: Concentrations of PM (above), levoglucosan and corresponding average VOC (middle) and temperatures inside the combustion chamber and of the hot flue gas (below) during the three combustions phases of 8 combustion cycles with hard wood

5.3.2.1 Influence of combustion temperature

Combustion temperature in this study is referred to the temperature measured inside the combustion chamber. There is a case with very high emissions of both PM and levoglucosan in the burn-up phase (the second cold-start cycle in Figure 52), which indicates bad combustion during the whole cycle. Nevertheless, a distinct evolution pattern of levoglucosan can be observed from the three combustion phases among all these cycles: a very high emission at the beginning of combustion process, which decreases during the combustion until very low or even zero emission at the burn-out phase. The concentration during the burn-up phase is one order of magnitude higher than those in the other two phases, especially in the cold-start cycles. Levoglucosan from burn-out phases shows the lowest emissions.

According to the formation mechanism of levoglucosan, taking into account the combustion mechanism of wood (Struschka, 1993), the evolution pattern can be interpreted by the effects from combustion temperature, which is measured as temperature inside the combustion chamber. At the burn-up phase, the temperature inside the combustion chamber is still relative low (see Figure 52, below), and this low temperature not only favors the production of pyrolysis products including levoglucosan, but also results in uncomplete combustion of these products during their residence time inside the combustion chamber. Therefore, a certain amount of unburned levoglucosan is emitted together with the hot flue gas and condensed on PM during travelling through the dilution tunnel in the burn-up phase. With the progress of combustion, the combustion temperature increases dramatically in a short time, which indicates the organic components in the pyrolysis gas could be burned out relatively well. Therefore, most of the levoglucosan produced during the main-burning phase is already destroyed under high temperature before being emitted with PM. At the end of the combustion cycle, the temperature is still relatively high, but the wood is almost burned through and no more gasification products are produced (Struschka, 1993). This leads to the very low emission of levoglucosan during the burn-out phase. To conclude, the emission of levoglucosan happens mostly during the first two combustion phases. The

higher the combustion temperature, the lower the emission levels of levoglucosan, and the evolution agrees with wood combustion mechanisms in the literature.

5.3.2.2 Influence of start mode

With regard to the cold-start cycles, levoglucosan is emitted at a much higher level during the burn-up phase than that in hot-start cycles (see Figure 52, middle). This result is correlated to the fact that cold-start cycles begin with a cold combustion chamber, which easily results in incomplete combustion and subsequently in higher emissions of unburned wood pyrolysis products, for example VOC, PAHs and intermittent products like levoglucosan. Therefore, the influence of cold start on levoglucosan emission is actually the influence of the combustion temperature as discussed above. This agrees also with the results from continuous sampling before and behind dilution discussed in Chapter 5.2. However, this trend is also observed for the other two combustion phases but not as consistent as that during the burn-up phase. Therefore, it is inferred that the influence of the cold start is limited to the first few minutes of the combustion cycle, and this factor becomes insignificant when the chamber temperature reaches a certain level, independent of other experimental conditions like airflow setting and wood type.

5.3.2.3 Correlation between levoglucosan and VOC

As discussed above, levoglucosan shows different emission levels during different combustion phases. Its correlations with corresponding VOC and temperature are discussed in detail here.

From Figure 52, it is observed that for all combustion cycles, high levoglucosan concentrations correspond to high VOC concentrations and low flue gas temperatures at burn-up phases. This is also true even for cycle 3, which has a very high levoglucosan concentration higher than 8000 $\mu\text{g}/\text{m}^3$ and a significant lower temperature inside the combustion chamber. The trend of the temperature through three combustion phases is reversed to that of VOC, for example, during the main-burning phase, the temperature is the highest and VOC is the lowest. This agrees well with the combustion mechanisms.

Results of levoglucosan and VOC and temperature inside the combustion chamber for three combustion phases from Figure 52 are shown again in Figure 53 (a) with a smaller coordinate dimension for a better observation (the two high concentrations of levoglucosan cannot be seen: $8516 \mu\text{g}/\text{m}^3$ and $5171 \mu\text{g}/\text{m}^3$). It can be observed that the difference between the trends of levoglucosan and VOC is that levoglucosan decreases further during the burn-out phase while VOC increases slightly. It is inferred that VOC is still produced and not completely burned at this phase with decreased temperature. But levoglucosan is mainly produced during the burn-up phase and is destroyed further even with slightly decreased combustion temperature during the burn-out phase.

The correlation between levoglucosan and VOC is shown in Figure 53 (b). For these 8 combustion cycles, levoglucosan increases in general with increasing VOC with a coefficient of 0.75. If the correlations are shown separately for different combustion phases in Figure 53 (c), a very high correlation of 0.97 is found in the burn-up phase when one point (levoglucosan: $5171 \mu\text{g}/\text{m}^3$) is treated as outlier. A closed value of 0.95 is attained for the burn-out phase while the value for main-burning is only 0.60. These three phases are shown again with a different coordinate dimension for a better observation in Figure 53 (d). It is clear that during the burn-up phase, higher amounts of VOC are emitted (higher than $400 \text{ mgC}/\text{m}^3$) compared to those from the other two phases. This big difference of VOC makes an obvious separation of the points between burn-up and the other two phases. As already pointed out before, levoglucosan from main-burning is in general a little bit higher than that from burn-out, while VOC shows an opposite trend. However, a high correlation is still found. To conclude, as VOC is an important variable reflecting combustion quality, this high correlation indicates that levoglucosan emission depends strongly on the combustion quality.

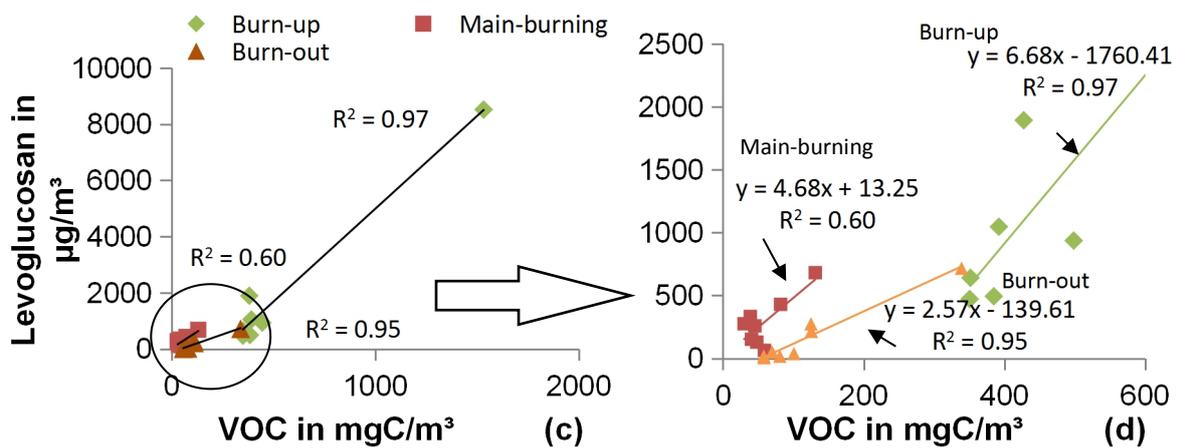
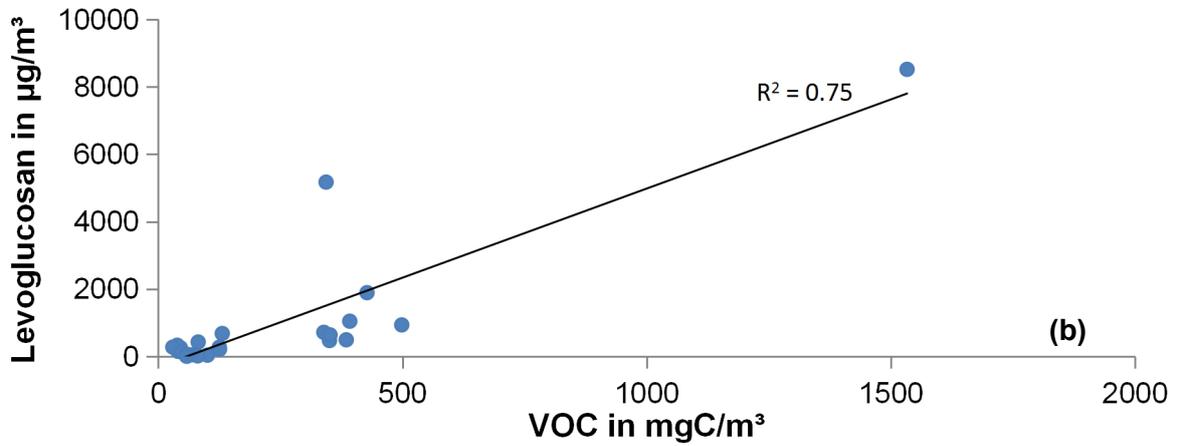
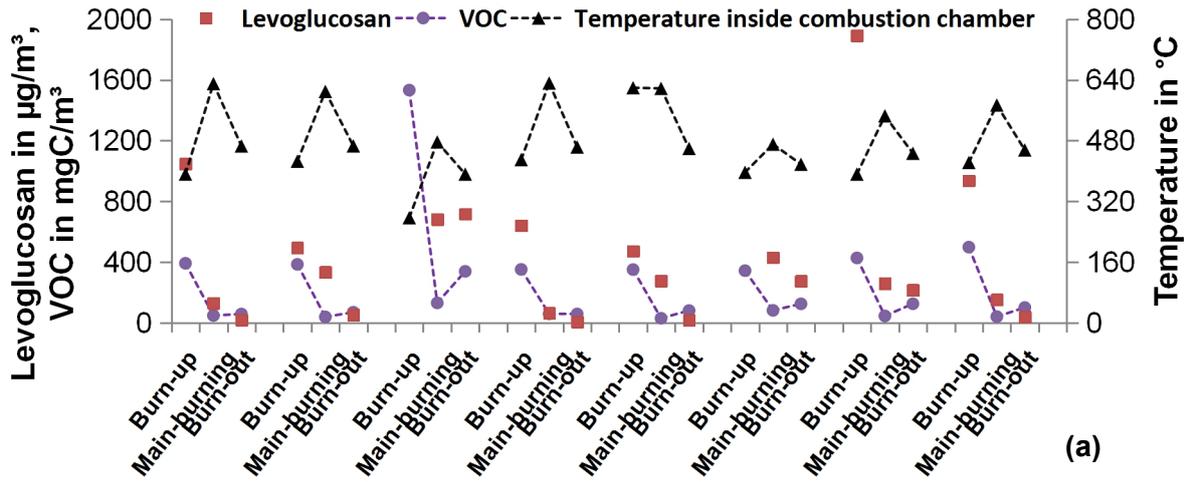


Figure 53: Results of levoglucosan and VOC and temperature inside the combustion chamber from 8 hardwood combustion cycles (a) and their correlation (b); (c) is (b) divided into three phases, with one concentration (5171 $\mu\text{g}/\text{m}^3$) from burn-up phase excluded as an ‘outlier’, (d) is (c) with a smaller coordinate dimension for a better observation.

5.3.2.4 Comparison of the correlation result with an odor-measurement project

The correlation between levoglucosan and VOC discussed above shall be compared to that found in a former project from Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart, where this study is also carried out. The main objective of this former project is to investigate the odor and PAHs emission from combustion of both hardwood and softwood in a wood stove (Struschka et al., 2013).

It is important to point out at first that due to different combustion units, operation conditions and other influencing factors, it is impossible to compare the results quantitatively. However, the trends of some parameters and the correlations between two parameters can be still compared in order to show the relevance of levoglucosan over VOC compared to odor over VOC. The first difference between the odor project and the levoglucosan study is that the combustion conditions in the odor project are divided into good combustion, bad combustion and worst combustion. Ignition phases are investigated in the odor project.

Nevertheless, only those combustion conditions, here referred to airflow setting on the stove, and combustion phases which were carried out in this study are compared here. The results of odor and VOC are shown in Figure 54. Odor was measured using the olfactometry method and the concentration is shown with the odor unit OU/m³. It can be seen that the highest emission levels of both VOC and odor are found in the burn-up phase with one exception under bad combustion. Odor concentrations are significant lower during the main burning phase and decrease further slightly at the burn-out phase, while VOC increases slightly from the main-burning phase to the burn-out phase during good combustion case. This agrees with the trend of VOC under both good and normal combustion in this study, which might indicate the division of good and normal condition in this study is not very distinctly and there is no significant difference in terms of combustion performance by varying this condition. That means, the variation caused by the two airflow conditions is relatively low compared to that in odor project, which leads to the results that levoglucosan and VOC emissions are independent of this variable as discussed in Chapter 5.2.2.

Nevertheless, irrelevant to airflow conditions, it is interesting to observe how similar the trends for levoglucosan and odor are, especially for VOC in both studies. This indicates that high emission levels of levoglucosan and odor could be expected when high VOC happens during the burn-up phase, which also suggests that these two parameters might be strongly correlated to each other. This finding should be of interest for future studies on this topic.

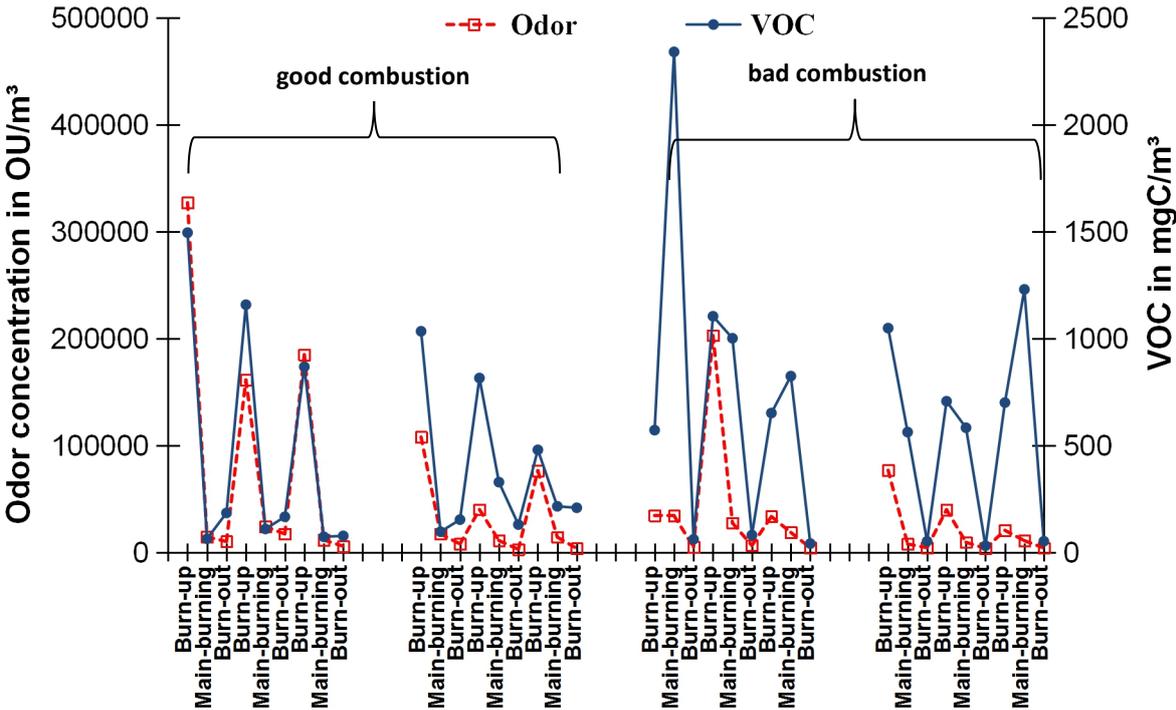


Figure 54: Odor and VOC concentrations during good and bad combustion in the odor project (Struschka et al., 2013)

Figure 55 shows the relative good correlation between odor and VOC under good combustion conditions with hardwood, which is the same kind of wood used in this study. This agrees with what we have found between levoglucosan and VOC with a correlation coefficient of 0.75 in Figure 53 (b). A relative poor correlation is found under bad combustion conditions, which is, however, not investigated in this study. It is therefore inferred that the emission of levoglucosan might have the same emission pattern as odor under good combustion conditions.

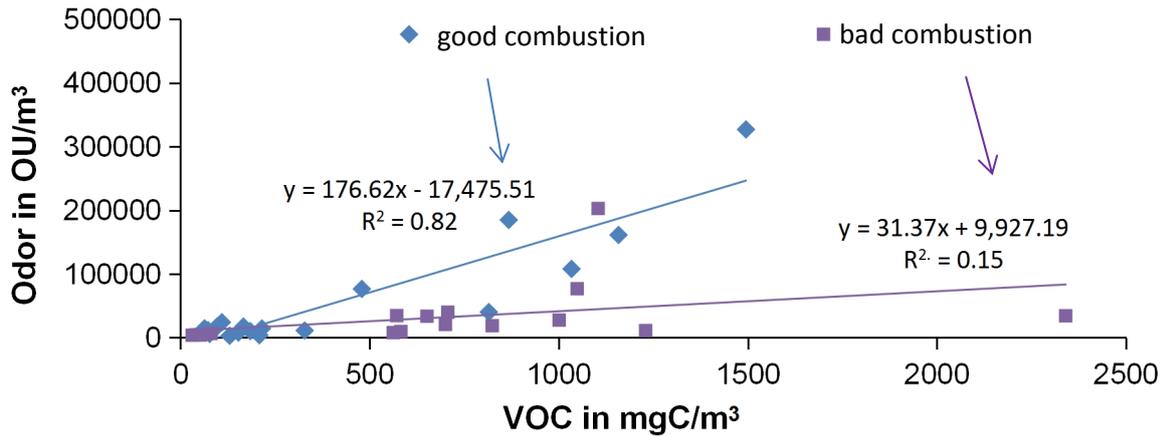


Figure 55: Correlation between odor and VOC for two combustion processes in the odor-project (hardwood, good combustion and bad combustion) (Struschka et al., 2013)

Similar results are also found for the correlation between odor and VOC in different combustion phases for hardwood. Correlations for the three phases under good combustion are 0.94, 0.41 and 0.00, respectively (Figure 56). This indicates that at burn-up phase, the emission of odor and VOC are strongly correlated, while the other two phases are in a small range (shown with a loop in Figure 56). The trends of emissions agree very well with those shown in Figure 53. Except that there are almost no correlations for odor and VOC at the burn-out phase while levoglucosan shows relative high correlation to VOC at the burn-out phase. This agrees with the combustion mechanism that there is no release of volatile compounds anymore and only the burning out of charcoal at this phase.

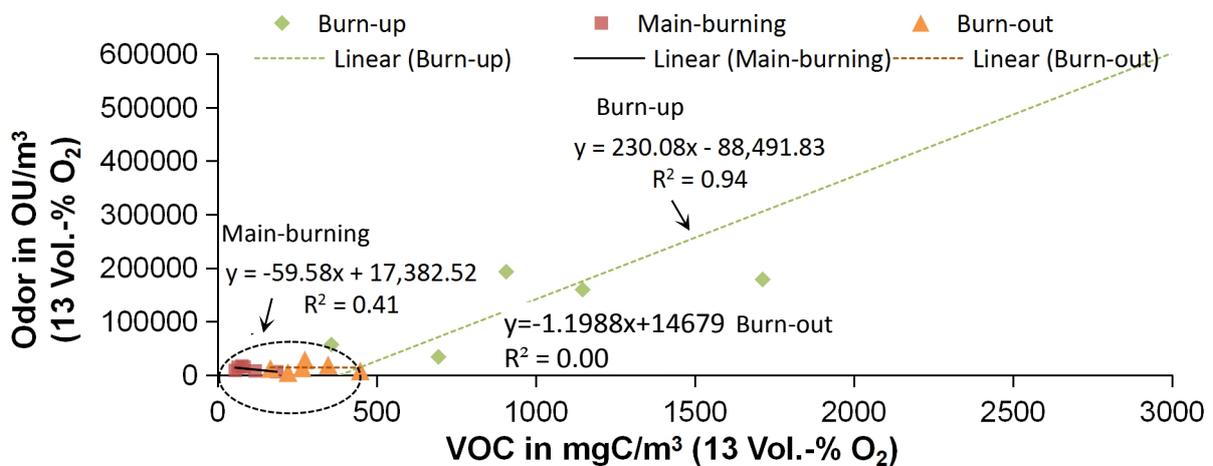


Figure 56: Correlation between odor and VOC during three combustion phases (good combustion) (Struschka et al., 2013)

5.3.2.5 Influence of dilution on levoglucosan emission

Correlation between levoglucosan and VOC has shown that emission levels of incomplete combustion products are emitted at different levels during the three combustion phases. According to the objectives of this study, the potential influence from different parameters on levoglucosan emission level has to be investigated in terms of dilution ratio and corresponding sampling temperature under certain combustion or operation conditions.

Performance of dilution technique

Different dilution techniques might achieve different ranges of dilution ratios. With regard to partial flow dilution, which involves usually commercial available dilutors, a wide range of dilution ratios can be achieved from several hundreds to thousands, which is very necessary for some sensitive devices with small measurement ranges. Partial flow dilution can also be realized by applying a dilution tunnel, whereby the achievable dilution ratio is significant lower than that from dilutors. An example is the stack sampling system brought out by Hildemann et al. (1989), which is applied by some other researchers in emission studies where the dilution ratios range mainly between 20 and 50 (Schauer et al., 1999; McDonald et al., 2000; Fine et al., 2001; 2004a). Another important function of a dilution tunnel is to simulate the cool down process in ambient air by applying it in a full flow dilution. Due to the large volume of full flow hot flue gas and the limited volume of a dilution tunnel, only a limited amount of dilution air can be applied and therefore dilution ratios are in a relative narrow range compared to those with partial flow especially in dilutors.

The dilution performance in terms of some parameters and corresponding results in this study are compared to some similar studies which applied a dilution technique for PM sampling from small combustion systems (Table 15). It can be seen that dilution tunnels in the listed studies are based on the EPA method or Norwegian Standard. Dilution ratios as well as sampling temperatures are within a small range even the objective of each study might be different.

In this study, the influence of dilution is to be investigated through varied dilution ratios and corresponding sampling temperatures. The dilution ratio can be adjusted in the range from 4 to 10, within which a sampling temperature range between 27 and 43 °C is attained. Both dilution ratio and sampling temperature are comparable to the values in the listed literatures, indicating the effective performance of this dilution tunnel.

Table 15: Comparison of dilution ratio and sampling temperature with literature

Dilution ratios	Sampling temperature °C	Dilution technique	Combustion units	Source
1.5 - 4.3	45 - 75	A full flow dilution tunnel	Pellet stove	Boman et al., 2011
	< 30	A dilution tunnel near ambient conditions according to the Norwegian standard	Domestic pellet heating system	Win et al., 2012
10	30 - 35	Dilution tunnel according to the Norwegian standard method (NS23058-2)	Fire place and wood stove (6 - 11 kW), stove and boiler (8 - 25 kW)	Ozgen et al., 2014
10 - 15	35	Dilution tunnel	Wood pellet stove	Toscano et al., 2014
-	-	Full flow dilution tunnel	Fire place and stove	Calvo et al., 2015
4 - 10	27 - 43	Full flow dilution with ambient air in self-constructed dilution tunnel based on EPA method	Log wood stove	This study

Dilution ratio and levoglucosan emission levels

In total three dilution ratios were applied for the performed experiments. A detailed investigation between the emission responses of levoglucosan to different dilution ratios shall be first discussed.

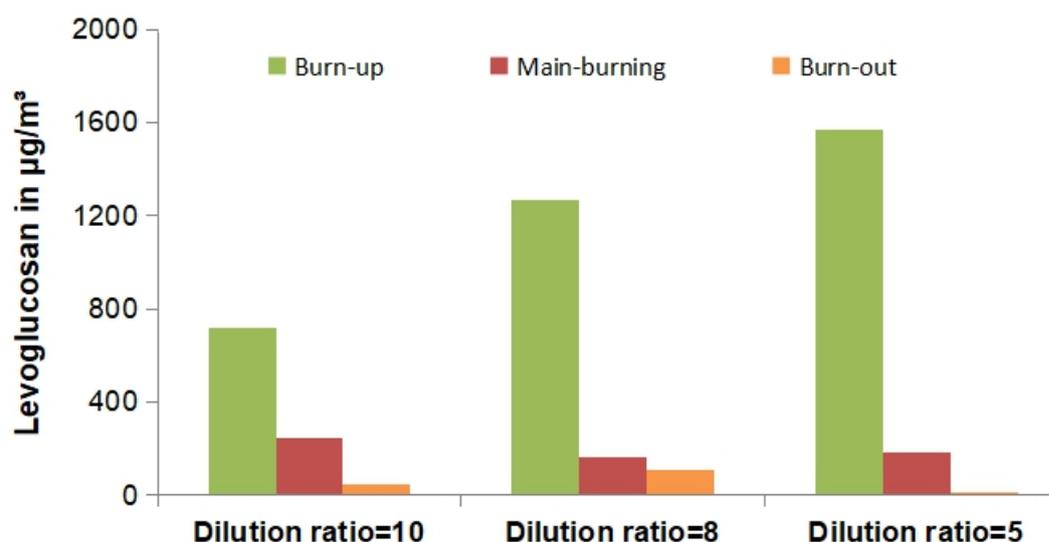


Figure 57: Average levoglucosan concentrations during three combustion phases under 3 dilution ratios (hardwood with hot start, 2 combustion cycles for each ratio)

In Figure 57 the levoglucosan concentrations during three combustion phases are compared between three different dilution ratios. Only the potential influence of the dilution ratio is of interest here and combustion condition is not taken as an experiment variable since cold-start as the main influencing factor is already eliminated here, and the influence of other combustion conditions on the measured amount of levoglucosan behind dilution is not obvious as discussed in Chapter 5.2.2. As can be seen in Figure 57, the levoglucosan emission during the burn-up phase shows an increasing trend with decreasing dilution ratios. However, this influence cannot be observed for the other two combustion phases. Nevertheless, under each dilution ratio, levoglucosan presents the highest concentration during the burn-up phase, in spite of the shortest sampling duration, followed by the main-burning phase, while the emission during the burn-out phase is the lowest. Therefore, it is

concluded here that the three dilution ratios show a difference only for the burn-up phase for given combustion conditions. But compared to the more significant differences which are observed between different combustion phases within the same ratio, the difference between the burn-up phases from different ratios can be considered as minor. In other words, in this study, combustion phases have a much higher influence on the emission response of levoglucosan than the dilution ratio. Based on the results from the performed experiment, a suggestion of a suitable dilution ratio might be not necessary. In this study, the ratio of 8 is chosen and used for the future experiments.

Sampling temperature and levoglucosan emission levels

Sampling temperature is referred to the temperature of diluted flue gas being sampled behind the dilution. This temperature is important and should be lower than the condensation temperature of levoglucosan, so that levoglucosan can be condensed on the particles and collected on the filters.

Based on the discussion above, the dilution ratio in the given range has shown no significant effect on levoglucosan emission levels for the performed experiments. The sampling temperature is, however, affected by both the dilution ratio and the temperature of the hot flue gas.

The average values of hot flue gas temperature before dilution (measured at point 1 at the combustion chamber exit, see Figure 44) and sampling temperature (measured at point 2 at the dilution tunnel) are shown in Figure 58. It can be seen that the temperature of the hot flue gas ranges between approximately 150 and 250 °C with one exception (a cold-start cycle which is shown separately due to its relative low temperature). The sampling temperatures for all the three phases during each combustion cycle are cooled down to 35 ± 8 °C with the three applied dilution ratios. Again, the corresponding sampling temperature during the cold-start cycle is also obviously lower than the average. Nevertheless, these sampling temperatures, which are actually the temperatures of the diluted flue gas, are all far below the condensation temperature of levoglucosan. The sampling temperatures are

reduced to a relative small range between different combustion phases, which implies that the dilution performance is relatively stable during the three sampling processes within these combustion cycles.

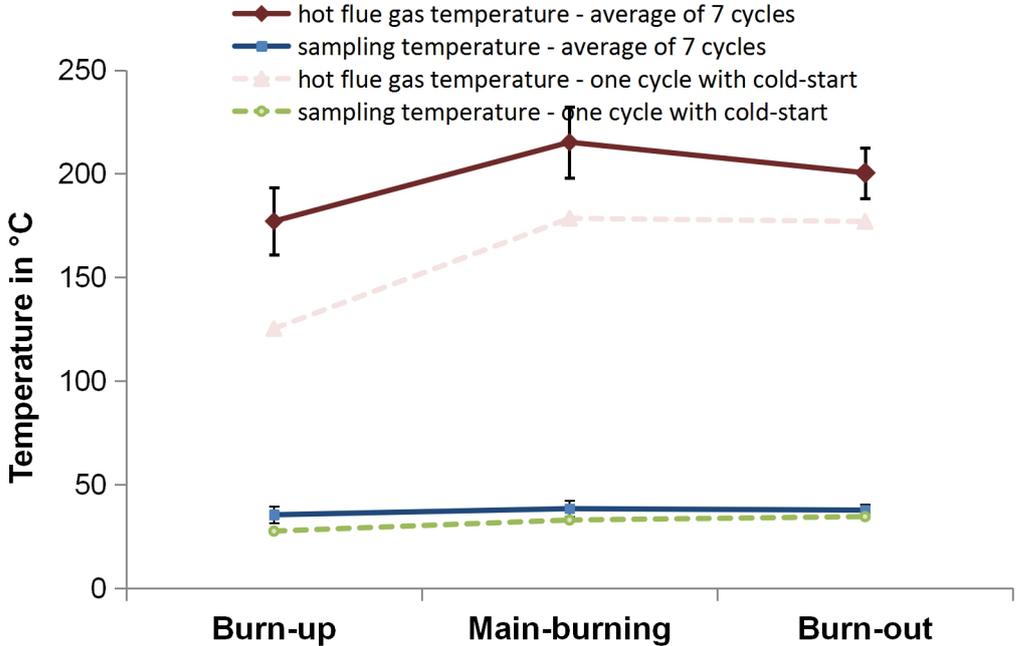


Figure 58: Average values of hot flue gas temperature and sampling temperature (diluted flue gas temperature) under three combustion phases (8 hardwood cycles, one cold-start cycle of hardwood is shown separately due to the relative low temperature)

The temperature of hot flue gas is directly affected by the temperature inside the combustion chamber. The influence of the combustion temperature on levoglucosan is already discussed before. The correlation between levoglucosan and the temperature of undiluted hot flue gas is shown in Figure 59. It can be observed that levoglucosan is inversely proportional to the temperature of hot flue gas at the burn-up phase with a relative high coefficient of 0.62. The levoglucosan levels during the main-burning phase are relative stable across the temperature range and no correlation is found (see highlighted part in Figure 59). A high correlation between levoglucosan and temperature is again found at the burn-out phase with a coefficient of 0.76. This indicates that a certain amount of levoglucosan is still not completely burned at the end of the combustion process, but the emission level is much lower than those in the other two phases.

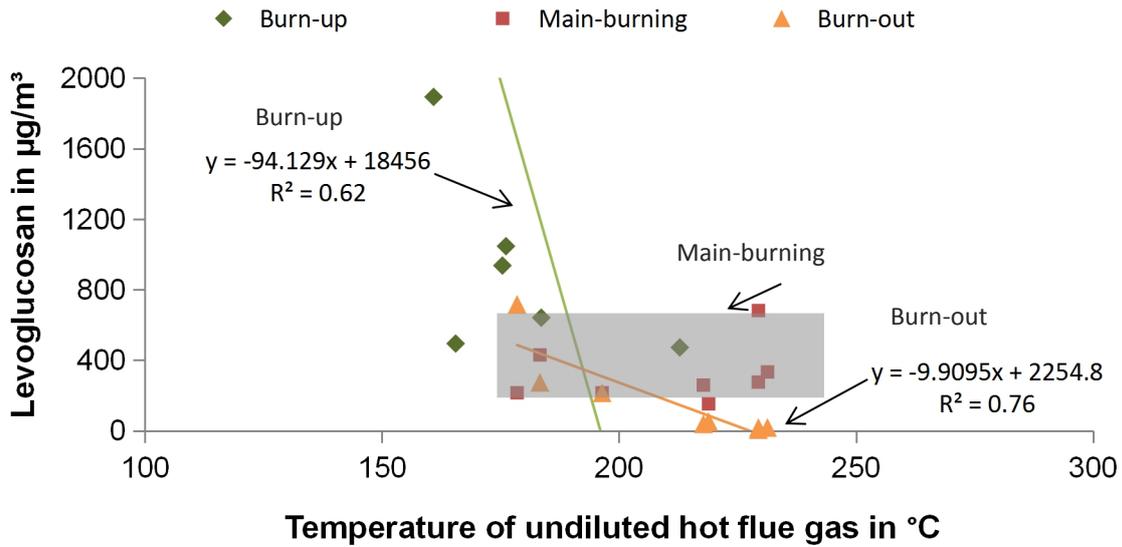


Figure 59: Correlation between levoglucosan (measured after dilution) and the temperature of undiluted hot flue gas (measured before dilution) for hardwood combustion cycles

The investigation of the correlation between levoglucosan and the sampling temperature is only possible when the input of levoglucosan in the hot flue gas is the same for all experiments. This is, however, unknown as no corresponding sampling of levoglucosan from the hot flue gas was performed. But as discussed before, levoglucosan is strongly correlated to VOC during the combustion process. Therefore, an attempt is made to sort the levoglucosan data based on comparable VOC values for each phase. The results are shown in Figure 60. It can be observed that levoglucosan levels are different under different sampling temperatures, but no significant correlation is found for all sorted data. This might be due to the fact that the sampling temperatures of diluted flue gas are reduced to about 35°C , varying within a relatively narrow range (between 30 and 50°C) compared to the temperature range of undiluted hot flue gas (between 150 and 250°C , see Figure 59), which has high correlations with the levoglucosan emission level for both burn-up and burn-out phases. This proves again the actual influencing factor is the hot flue gas temperature as well as the temperature inside the combustion chamber, which is decisive for the formation and subsequent emission of levoglucosan.

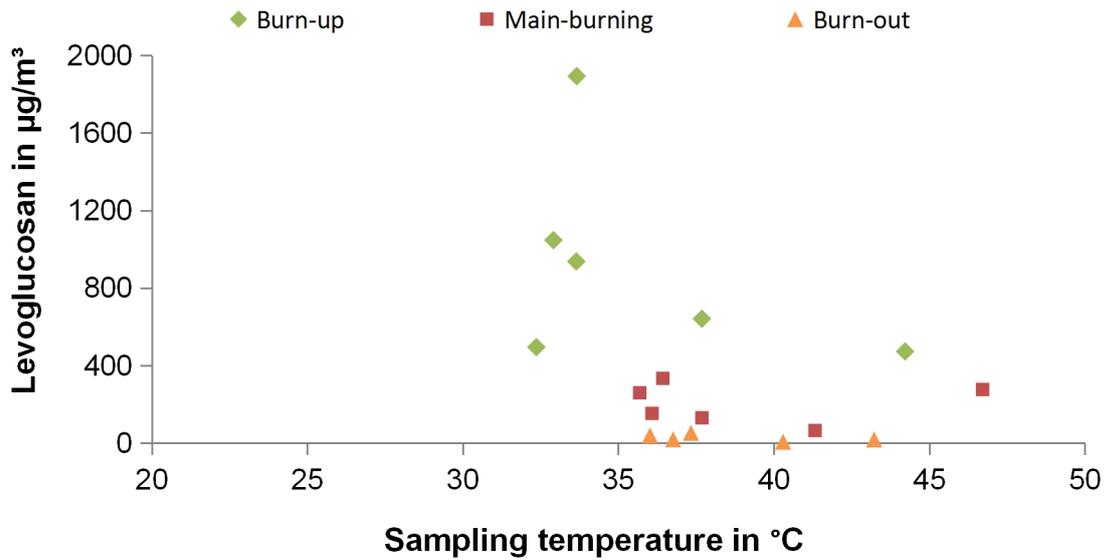


Figure 60: Correlation between levoglucosan and sampling temperature

To sum up, the emission level of levoglucosan from wood burning has a strong inverse correlation with the combustion temperature resp. hot flue gas temperature. The sampling temperatures vary within a small range, which means they are all lower than the condensation temperature of levoglucosan. In this way, a certain amount of gas-phase levoglucosan condenses on the particles and can be collected on the filters. Therefore, the dilution has a cool down effect on the hot flue gas and plays an important role on the condensation of levoglucosan. But the measured amounts of levoglucosan from filters are not correlated to the specific sampling temperature for the performed experiments. Similar results regarding PAHs are found by Boman et al. (2005). He concluded that no influence of the sampling temperature is observed for the total PAH or the dominating PAH compounds.

5.3.3 Results of softwood combustion

In the combustion cycles with softwood, the levoglucosan concentrations from two hot-start cycles are lower than those from the cold-start cycle, which agrees with the observation of the hardwood case in Figure 52. However, the levoglucosan concentrations show different trends during the three combustion phases and no pattern could be found between the burn-up phases within the three cycles. It is also surprising to see that levoglucosan levels during main-burning and burn-out phases are significantly higher than those in the corresponding phases for hardwood under the same experimental conditions in term of airflow. It is inferred that this might be partially due to the different compositions between hardwood and softwood. Another reason might be that there is a difference between the average combustion temperatures from these two wood types (see Figure 51). Combining the corresponding high concentrations of CO and VOC in Figure 61, it seems that the slightly lower temperature from softwood burning is correlated to bad combustion quality since CO and VOC are indicator of incomplete combustion. Therefore, the difference of the combustion temperatures could be responsible for the difference in the levoglucosan level between the two wood types. An explanation for the very high levoglucosan concentration during the main-burning phase in the cold-start cycle is actually due to the relative bad combustion quality, which could be proved by the very high concentrations of CO and VOC.

For the softwood case, it is summarized that levoglucosan is also produced during all three combustion phases and the concentrations are significantly higher than those from hardwood burning, but no significant trend is observed during the different phases, which might be also due to the limited amount of combustion cycles investigated. In this study, the results for softwood are only used for the calculation of emission ratios of levoglucosan for source apportionment but are not taken into account in other discussions.

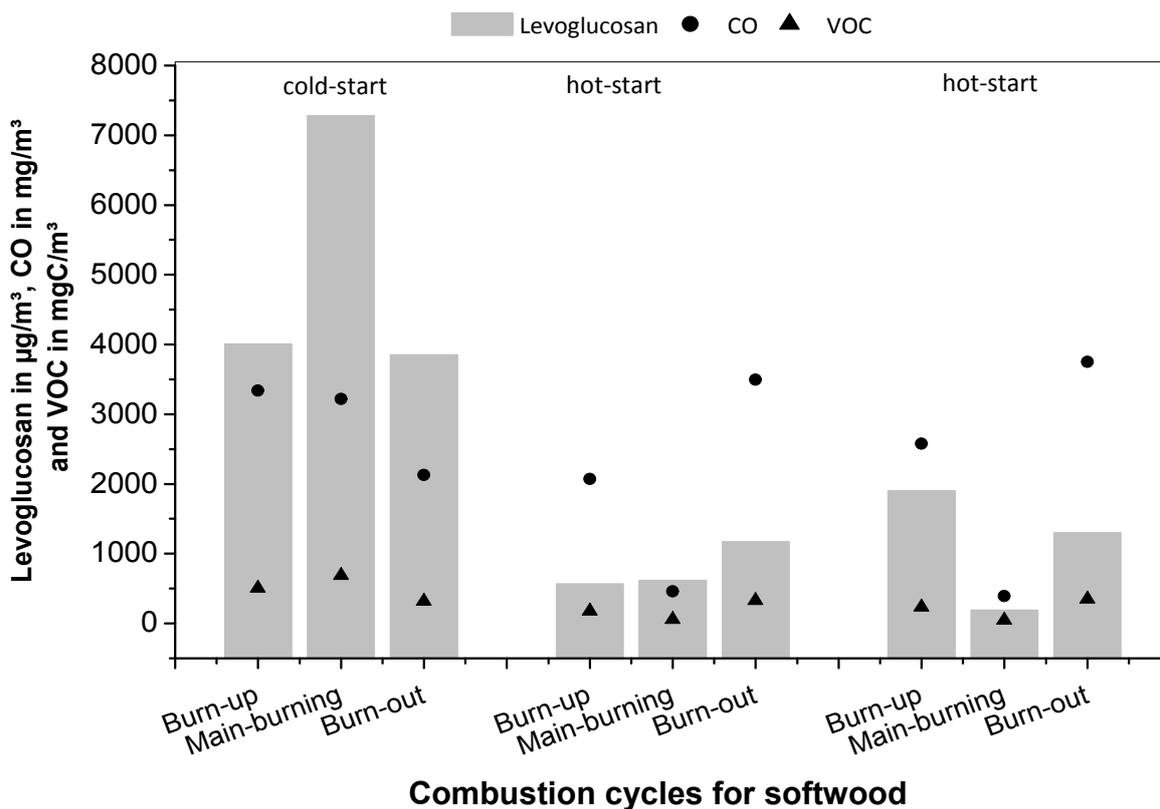


Figure 61: Levoglucosan concentrations with corresponding CO and VOC during three combustion phases (softwood, three combustion cycles)

5.3.4 Summary of combustion phases sampling

Levoglucosan from combustion phases sampling can be concluded in several points. First of all, levoglucosan is mainly produced during the burn-up phase and partially during the main-burning phase. Secondly, a dilution ratio between 5 and 10 is sufficient to cool down the hot flue gas to an average temperature of 38 °C, which results in the condensation of levoglucosan on PM which can be collected on filters successfully. Furthermore, levoglucosan is detected with high concentration during the burn-up phase, regardless of combustion conditions. The sampling conditions (dilution ratio within the range from 5 to 10) seem to have an effect on the emission level, but the differences between the cycles with different dilution ratios are not so significant when compared to those between burn-up phase and the other two phases. A cold start is correlated to a low combustion temperature and therefore causes a high amount of levoglucosan during the burn-up phase.

5.4 Emission ratios of levoglucosan to PM

"Emission ratio" in this study is referred to the ratio of levoglucosan mass over PM mass base shown in percentage (levoglucosan/PM in %, w/w, see also Chapter 2.3.2), both determined from the filters collected behind dilution. The most important aim in this emission study is to attain a specific emission ratio of levoglucosan based on local-used wood types and wood stoves. However, experimental results have shown that emission levels of both PM and levoglucosan vary greatly from test to test. The variation of the levoglucosan emission ratio could be very significant. Therefore, this attempt is adjusted to attain a range of emission ratios, which could be applied for the source apportionment.

Based on the measured values at the end of dilution tunnel as discussed in Chapter 5.2 and Chapter 5.3, emission ratios of hardwood and softwood could be calculated for the performed experiments. The application of the calculated emissions ratios for source apportionment of ambient PM is discussed in Chapter 6 later.

5.4.1 Emission ratios from combustion phases sampling experiments (hardwood)

Calculation of the levoglucosan emission ratios from combustion phases sampling cannot be carried out directly since the sampling process for each combustion cycle is not continuous over the whole cycle but divided into three parts according to the three combustion phases: burn-up, main-burning and burn-out. Moreover, the sampling duration has not covered the actual duration of each phase. Theoretically, if the actual duration of each phase is known, the results could be attained by using the weighted average levoglucosan (integration content of levoglucosan) sampled from each phase over the corresponding phase duration, which is then divided by PM mass attained in the same way for each combustion cycle. However, there is so far no standard definition for the division of specific duration for each combustion phase regarding residential wood burning. In this study, the mentioned three phases are identified according to the CO₂ content in hot flue gas during the combustion as mentioned in Table 11. Based on the CO₂ profiles for all valid experiments, the range of the durations for each combustion phase are observed and the results are shown in Table 16.

Table 16: Observed range of phase duration for the performed combustion cycles

Phase	Burn-up	Main-burning	Burn-out
Range of CO ₂ content (Vol.-%)	<3	>10	<5
Observed range of duration (minutes)	3-6	6-15	6-10
Actual sampling duration (minutes)	3	6	6

As phase durations are different from test to test, in order to find a suitable duration for each phase, several durations within each corresponding range are selected and calculated for the corresponding ratios of levoglucosan to PM in order to observe the variations. The calculated ratios of levoglucosan over PM starts with the burn-up phase, which are based on the varied duration of this phase and the actual sampling durations for the other two phases (Table 17). The results from varied durations are compared to the results calculated based on actual sampling durations which are shown in bold values in Table 17.

Table 17: Emission ratios of levoglucosan based on different selections of phase durations (hardwood with partial load, measured after dilution from 10 combustion cycles)

Phase (minutes for 3 phases)		Burn-up (x, 6, 6)			Main-burning (3, x, 6)			Burn-up (3, 6, x)		
Selected durations for this phase (x:minutes)		3	5	6	6	10	15	6	8	10
Levoglucosan/PM (% w/w)	cold start	13.3	14.0	14.2	13.3	12.8	12.4	13.3	13.2	13.0
	hot start	3.8	4.4	4.6	3.8	3.3	3.0	3.8	3.7	3.6
	average	6.6	7.2	7.5	6.6	6.2	5.8	6.6	6.5	6.5
Mass of levoglucosan and PM calculated from the whole sampling process										
Levoglucosan (µg)	average	521	797	935	521	569	628	521	534	546
PM (mg)		8.3	10.7	11.8	8.3	10.8	14.0	8.3	8.6	8.9

Results show that for the burn-up phase, a 3-minute longer duration results in a higher ratio in both start mode cases. The overall emission ratio increases from 6.6 to 7.5. For the main-burning and burn-out phase, the increasing sampling duration results in smaller ratios in both start modes. When the durations increase from 6 to 10 minutes, the average emission ratios decrease from 6.6 to 6.2. But with the same time extension, the variation in the burn-out phase is smaller than that in the main-burning phase. This indicates that the duration of the burn-out phase is not decisive due to the relative low emission in this phase. Nevertheless, these differences are actually very small compared to the difference between the two start modes. It seems that the determining factor for the emission ratio is the start mode, namely the cold start. Durations for each phase especially for the main-burning and burn-out phase have very little influences on the results. Therefore, the middle values for each phase in Table 17 are chosen as durations for the determination of emission ratios. This means, 5 minutes for the burn-up phase, 10 minutes for main-burning and 8 minutes for burn-out. Based on this combination of durations, the emission ratios are calculated as 3.8 % for hot start and 13.4 % for cold start, with an average emission ratio of 6.7 %, These results are slightly higher than those calculated from the actual sampling durations (Table 18).

Table 18: Average emission ratios of levoglucosan with corresponding concentrations of levoglucosan and PM from combustion experiments with phases sampling after dilution

Phase durations for three combustion phases (minutes)		(chosen durations) 5, 10, 8	(actual sampling durations) 3, 6, 6
Levoglucosan/PM (% w/w)	cold-start	13.4	13.3
	hot-start	3.8	3.8
	average	6.7	6.6

5.4.2 Emission ratios from continuous sampling experiments (hardwood and softwood)

Emission ratios of both hardwood and softwood from the experiments with continuous sampling before and behind dilution are calculated and present as average values on weight basis in Table 19. The corresponding concentrations of levoglucosan and PM are also listed for a better understanding. In the hardwood case, cold-start experiments have an average emission ratio of about 10 % w/w, while the one for hot-start experiments is about 8 % w/w. An overall average for all hardwood tests is 9.0 % w/w, which is very close to the result from Schmidl et al. (2008) who found a weight average levoglucosan/PM ratio of 9.3 % w/w in wood smoke .

In softwood case, results are only shown for an overall average without separation of different start mode. It can be observed that variation of softwood levoglucosan is relative high and the average is double as high as that from hardwood. A detailed comparison of these ratios with other studies is presented in Chapter 5.4.3.

Table 19: Average emission ratios of levoglucosan with corresponding concentrations of levoglucosan and PM from combustion experiments with continuous sampling

		Hardwood	Softwood
Levoglucosan/PM (% w/w)	cold-start	10.3 (6.5 - 15)	
	hot-start	7.6 (1.1 - 23.9)	
	average	9.0	19.1
Levoglucosan ($\mu\text{g}/\text{m}^3$)	cold-start	3681	
	hot-start	849	
	average	2265	1420
PM (mg/m^3)	cold-start	31.31	
	hot-start	17.37	
	average	24.34	6.2

5.4.3 Comparison of levoglucosan emission ratios to literature values

Based on the results from Chapter 5.4.1 and Chapter 5.4.2, emission ratios of hardwood from experiments with continuous sampling method are 10.3 % w/w for cold-start and 7.6 % w/w for hot-start, with an overall average of 9.0 % w/w (Table 19), while the results from experiments with combustion phases sampling are 13.4 % w/w for cold-start and 3.8 % w/w for hot-start with an average of 6.7 % w/w (Table 18). These ratios, irrelevant of sampling technique, are comparable to those found in the literature in and outside Europe as listed in Table 20.

From these studies, relative constant levoglucosan emission ratios are found within the range between 5 and 15. The results of 9.0 % w/w for hardwood from continuous sampling is relative close to the result from Schmidl et al. (2008).

In the softwood case, a higher average of 19 % is found in this study. This result seems to be not consistent with the findings in the studies from Fine and his co-workers, where they found that softwood tended to exhibit lower emission of levoglucosan than hardwood (Fine et al., 2001; 2002a). However, similar results are found in the study from Schmidl et al. (2008), where he also found high variability of levoglucosan content in PM from softwood spruce smoke, which varied from less than 1 % to as high as almost 18 %, with an average of 14 % for those tests with high emission. Besides, a value of 15 % is found for softwood Larch, while lower emissions are found for hardwood Beech and Oak (4.1 % and 13.3 %, respectively). Therefore, the value of 19 % in the softwood case seems not be absolute unreasonable, but more tests should be carried out for a better evaluation in a future study.

Table 20: Emission ratios of levoglucosan to PM mass for wood smoke in literature (studies in Europe or outside Europe)

Levoglucosan/PM % w/w	Wood type	Combustion units	Literature
13.4 (3.8-19.1) Softwood: 19.1 Hardwood: 8.8 (cold-start: 10.3-13.4 hot-start 3.8-7.6)	hardwood and softwood	a manually fired stove	This study
11.3 (0.8-31.8)	calculated from literature data	species in Lombardy, Northern Italy	Piazzalunga et al., 2011
5 (Oak 8.2 Beech 2 Spruce(sw) 5.5 Briquettes (sw) 2.5)	hardwood and softwood	manually fired stoves	Schmidl et al., 2011
9.3 (4-15) (Beech 4.1 Oak 13.3, Spruce 10.7, Larch 15.1 Briquettes 10.1)	common mid- European wood types mixed	a typical domestic tiled stove for Austria	Schmidl et al., 2008
14 (5-16)	locally available wood	wood heater with a dilution tunnel apparatus based on AS/NZS 4013:1999	Jordan and Seen, 2005

*Units; mg g⁻¹ organic carbon (OC) emitted

5.5 A suitable sampling procedure for levoglucosan

The studies regarding combustion mechanisms in laboratory scale reveal some boundary conditions for levoglucosan formation (Kuo et al., 2008). However, this finding is limited to controlled experimental conditions, which does not reflect the realistic situation. In reality, wood combustion inside a wood stove is more complicated since it takes place normally in manually operated stoves. The emission of pollutants can be affected by many unpredictable factors. Therefore, the study of levoglucosan emissions from wood combustion in representative wood stoves is of great importance since it reflects more realistic operation conditions. The results of levoglucosan from emission studies can be applied to the tracer method for the evaluation of the wood burning contribution into ‘real world’ ambient pollution. This application will be discussed in chapter 6 for the source apportionment study.

Based on the results and discussions of levoglucosan sampling from the performed experiments (from Chapter 5.2 to Chapter 5.4), some sampling conditions are summarized and suggested as a suitable sampling procedure for levoglucosan with regard to the applied dilution tunnel in this study.

Dilution ratio and sampling temperature

The listed studies regarding levoglucosan sampling with dilution in Table 15 have shown that dilution ratios are mainly between 5 and 10, and the sampling temperature mainly within the range from 20 to 45 °C. In this study, levoglucosan is successfully sampled and measured from filters when hot flue gas is diluted and cooled down to between 27 and 43 °C. This indicates that within this temperature range, the sampling temperature is not a critical parameter for the detected amount of levoglucosan. In other words, the length of the dilution tunnel in this study is sufficient to fulfill its function and it could be applied for future experiments with a dilution ratio between 5 and 10.

Sampling duration

Previous results show that most of the levoglucosan is emitted mainly during the burn-up phase and partially during the main-burning phase. The percentage of levoglucosan from these two phases over the total amount from three combustion phases can be quantitatively determined by summing up of the amount of levoglucosan from each filter (in μg). Results show that levoglucosan from the first two phases represents more than 90 % of the total levoglucosan from all three phases (Table 21).

Table 21: Average percentages of levoglucosan from the burn-up and main-burning phase to the total levoglucosan from all three phases (hardwood combustion)

	Cold-start	Hot-start
Percentages (%)	93.3	94.4
(range)	(91.7 – 97.3)	(84.9 – 99.7)
Overall average (%)	94.0	

A minor difference is found between the two start modes, but the difference is really small taking into account the variation range. An overall average of 94 % is attained. Therefore, the emission from the burn-out phase accounts for only about 6 %. This gives a direction for a rough evaluation of levoglucosan emission from wood burning: sampling of PM-bound levoglucosan at the burn-up and the main-burning phase may be representative.

Regarding the durations of these two phases, based on the discussion about Table 17 in Chapter 5.4.1, a 5-minute duration is chosen for the burn-up phase and a 10-minute duration for the main-burning phase. Therefore, if a continuous sampling is to be carried out, the sampling duration can be decided to be the first 15 minutes of the combustion process, which is believed to cover the whole burn-up phase and if not all, at least a large part of the main-burning phase. In this way, the collected levoglucosan can be also expected to account for a share of the total amount up to about 94 % as shown in Table 21. Based on this result, the emission ratio of levoglucosan can be also estimated for source apportionment.

These sampling conditions regarding using a dilution tunnel can be suggested as a suitable sampling procedure for levoglucosan sampling at emission sources in future studies.

6. Wood burning contribution to ambient PM₁₀

In this study, measurements of ambient air pollutants were carried out in a residential area in winter 2013/2014 and winter 2014/2015. The results are discussed in terms of air pollutants and levoglucosan in Chapter 4. Emission research regarding sampling of levoglucosan direct at a wood stove was investigated and the emission ratios of levoglucosan at emission sources were calculated (Chapter 5). By combining these data, it is possible to calculate the share of PM emitted from residential wood burning, which cannot be measured directly continuously since the total ambient PM cannot be separated physically. The process to calculate the PM contribution from residential wood burning to local ambient PM₁₀ in the investigated area is the so-called source apportionment. In this chapter, the apportionment of local PM₁₀ is carried out by the levoglucosan tracer method based on the previous results from levoglucosan. The calculated results are discussed and compared to literature values.

6.1 Calculation procedure for the levoglucosan tracer method

6.1.1 Review of the method

The application of using levoglucosan as mono-tracer for calculating wood burning contribution to local ambient PM₁₀ in this study is referred to the calculation method described in the publication from Schmidl et al. (2008). The application principle and the calculation procedure are already discussed and shown in detailed in Chapter 2.3.2. It will be reviewed briefly below.

In order to quantify the wood burning PM in ambient air, total ambient PM₁₀ and PM-bound levoglucosan should be measured at a receptor site. Emission ratios of levoglucosan for different local-used wood types can be determined by measurements of levoglucosan in the flue gases directly at an emission source before it is emitted into the ambient air. The knowledge about the local wood consumption structure in an investigated area is also required for the derivation of a conversion factor according to Schmidl et al. (2008). If the conversion factor is attained, together with the mass of levoglucosan measured in ambient

PM samples, wood burning PM can be calculated. The specific calculation procedure is referred to Chapter 2.3.2. Some important formulae are shown again below.

6.1.2 Determination of a local conversion factor

Wood burning PM in ambient air can be calculated according Equation 2.6.

$$M_{\text{WBPM, amb}} = M_{\text{Levo, amb}} \times F_{\text{loc}} \quad \text{Equation 2.6}$$

Where $M_{\text{Levo, amb}}$ and $M_{\text{WBPM, amb}}$ are the mass of levoglucosan and wood burning PM collected on the filter over a certain sampling period at a receptor site inside a residential area, respectively, and F_{loc} is the local conversion factor defined as Equation 2.5 according to Schmidl et al. (2008).

$$F_{\text{loc}} = 100 \% / \sum (P_i \times ER_i) \quad \text{Equation 2.5}$$

Where ER_i is the emission ratio of levoglucosan from wood types i (% w/w) and P_i is the relative percentage (%) of wood type i in the total wood consumption structure in the residential area (Schmidl et al., 2008).

Therefore, with available ambient data of levoglucosan, wood burning PM can be calculated if P_i and ER_i are known. However, a common issue for determining the conversion factor in source apportionment studies is that information about wood consumption structure is unknown and exact data could not be attained. Schmidl et al. (2008) recommended a wood combination (70 % spruce, 20 % beech and 10 % briquettes) in his study based on some available information and the actual situation in Austria. In the study from Piazzalunga et al. (2011), he took a few emission factors from literature and conducted a weighted factor according to the partially known data about wood consumption structure in Lombardy.

In this study, as already mentioned before, the wood consumption structure in the investigated area is relative simple with only two wood types (Table 10), one is beech wood (hardwood, hw as subscript) and the other is spruce (softwood, sw as subscript). Therefore, the local conversion factor from Equation 2.5 could be calculated as:

$$F_{\text{loc}} = 100 \% / (P_{\text{hw}} \times ER_{\text{hw}} + P_{\text{sw}} \times ER_{\text{sw}})$$

Where $P_{hw} + P_{sw} = 100 \%$, and emission ratios of levoglucosan from hardwood ER_{hw} and from softwood ER_{sw} are already attained in Chapter 5 (Table 18 and Table 19), but specific values for the relative percentage of these two wood types (P_{hw} and P_{sw}) are unknown.

Different from the situation in Austria, people in this region consume a much higher share of hardwood than softwood due to wood availability according to the previous study from Bari et al. (2010), where it is mentioned that hardwood used for residential heating is more than 90 % of the total firewood and this was confirmed by the official local chimney sweeper. Based on this singly available information, it seems unreasonable to derive just a single value as the conversion factor. Instead, it should be much more close to reality to derive a range by suggesting different scenarios for the local wood consumption structure. That is, there are various combinations of hardwood and softwood share, where hardwood share is assumed to be changed from 80 % to 95 %, with corresponding softwood share varying from 20 % to 5 %.

Emission ratios from hardwood and softwood are listed in Table 22. It can be seen that softwood has only one average value while for hardwood there are individual values for cold and hot-start, with an average of 11.7 for cold-start from two sampling methods and an overall average of 7.7. These two average values and the emission ratio from softwood are applied together with the consumption scenarios to Equation 2.5, which result in a series of conversion factors (Figure 62). This process could be also considered as a sensitivity investigation of the conversion factor to the different percentage of each wood type.

Table 22: Emission ratios of levoglucosan determined from hardwood and softwood

Wood type	Experiment method	Emission ratios of levoglucosan based on PM (% w/w)		
		Cold-start	Hot-start	Average
hardwood	continuous sampling	10.3	7.6	9.0
	combustion phases sampling	13.4	3.8	6.7
	average	11.7	5.2	7.7
softwood	continuous sampling			19.1

It is clear that the local conversion factor varies when there is a change in the share of the wood type. Generally, the conversion factor increases slightly with increasing hardwood share with 5 % intervals. This indicates the variation of wood consumption structure within a narrow range shows no significant influence on the conversion factor. Instead, the difference between cold-start average and the overall average is higher, which is about 4 (12.1 to 8.3) at a hardwood share of 95 %. Therefore, the cold-start mode should be taken into account when deciding the final range for a conversion factor. On the other hand, the factor should also agree with the local wood consumption structure situation. Based on these considerations, the lower factor from 85 % which is derived from cold-start average emission ratio of 7.8 and the higher factor from 95 % which is from the overall average emission ratio of 12.1 are chosen as the lower and upper value of the range, respectively.

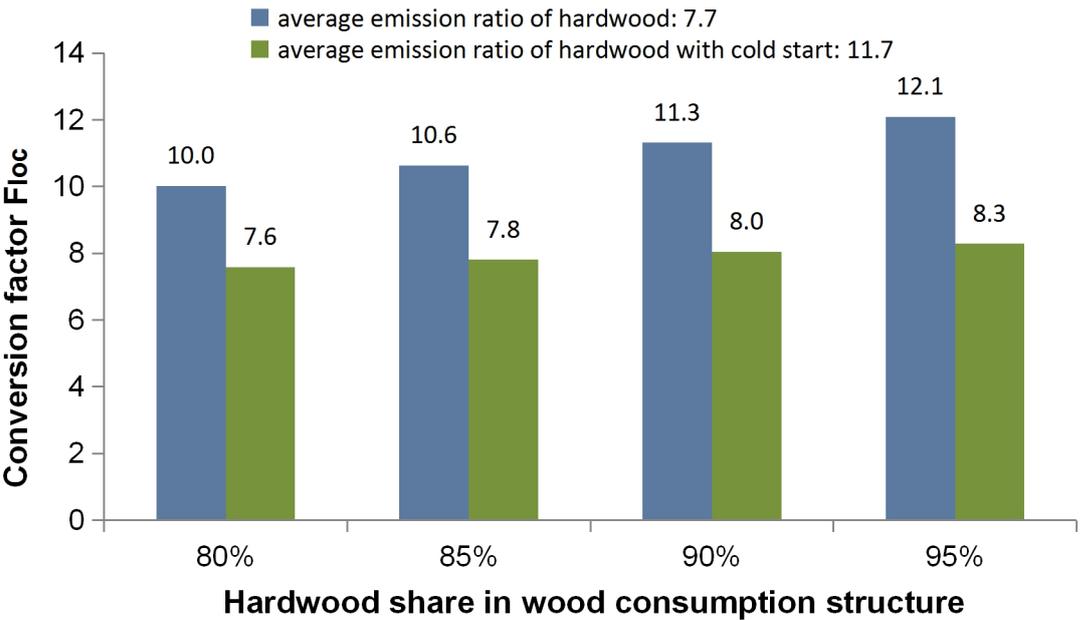


Figure 62: Sensitivity analysis of the conversion factor based on various combinations of hardwood and softwood in the consumption structure

Some apportionment studies carried out across Europe (mainly in central and northern Europe) are compared to the own results in Table 23. Before the comparison, it is important to point out that most of the studies in literature apply simply a factor for the calculation based on a single emission ratio of levoglucosan without taking into account the wood

consumption structure. Attentions should also be paid to the fact that these factors are derived based on different mathematic methods. Studies which have taken factors from other literature are not included here.

Factors listed in Table 23 are within a certain range except the very high value of 71 from LUBW (2016) and the relative high one from Helsinki. The two factors derived in this study are comparable to the results from Austria, Nordrhein-Westfalen and Portugal, while the average of 10 is relative close to that from Schmidl et al. (2008).

Table 23: Factors of levoglucosan for the calculation of wood smoke contribution to ambient PM₁₀ in literature

Factor	Derivation methods	Studied area/ Site characterization	Source
10.0 (7.8 - 12.1)	Measurement of the emission from a wood stove with both hardwood and softwood	Dettenhausen, Germany	This study
71	Determined from wood stove at a test stand	Baden- Wuerttemberg, Germany	LUBW, 2016
13	Day-evening measurement of ambient levoglucosan	North Rhine- Westphalia, Germany	Pfeffer et al., 2013
24 ± 9	Derived from ambient-environment studies	Helsinki Metropolitan Area, Finland	Saarnio et al., 2012
8.6	Calculated from ambient data	Baden- Wuerttemberg, Germany	LUBW, 2010
7.9	Calculated from ambient data	Augsburg, Germany	Bayerisches Landesamt für Umwelt, 2009
10.7	Emission experiment of 5 commonly local used wood	Austria	Schmidl et al., 2008

6.2 Results calculated from conversion factors

After the derivation of the local conversion factors in Chapter 6.1, these values can be applied in the Equation 2.6 to calculate the wood burning PM in ambient air. Subsequently, the contribution of wood burning PM to total ambient PM₁₀ in the studied area can be calculated by dividing wood burning PM by the total ambient PM₁₀, both referred to the mass collected on the filter samples.

The ambient-measurement data during winter 2014/2015 are calculated firstly with the factor of 7.8 and the results are shown in Figure 63. Wood burning PM is presented here as concentration in $\mu\text{g}/\text{m}^3$. It can be seen that the concentrations of wood burning PM vary significantly through the measurement period. An average concentration over the whole winter is calculated as $3.0 \pm 2.4 \mu\text{g}/\text{m}^3$. The corresponding wood burning contributions (in %) show also strong variations. Some relative high contributions are observed, which happened during inversion periods. Therefore, these high contributions can be partially attributed to the influence of this weather condition. Two very high contributions (57 % and 52 %) are found from the samples collected during the Christmas holiday and from 4th to 6th January 2015, which are public holiday periods in this area. Therefore, the high values might be explained by intensive heating behavior with wood burning from residents during this holiday period. Since these high values do not represent a normal emission case, they are excluded for the calculation of an average of wood smoke contribution but mentioned separately. An average contribution of 16 % is attained with the conversion factor of 7.8.

The contribution calculated with the conversion factor of 12.1 has a similar trend (Figure 64). With this higher factor, it is not surprising to see that the calculated concentrations of wood burning PM are having higher values and the corresponding contributions are also higher than those from Figure 63. The corresponding average concentration in Figure 64 is calculated as $4.7 \pm 3.7 \mu\text{g}/\text{m}^3$ with a conversion factor of 12.1. It is also worth to mention that the very high contributions during holidays are here as high as about 80 % (Figure 64). This seems to be unreasonable and again this value is excluded for calculation of wood burning contribution. Subsequently, an average of 25 % is calculated for the contribution in

this case. It is therefore to conclude that based on the two chosen factors, the average contribution to total ambient PM₁₀ from residential wood burning ranged from 16 to 25 % in the investigated area during winter 2014/2015.

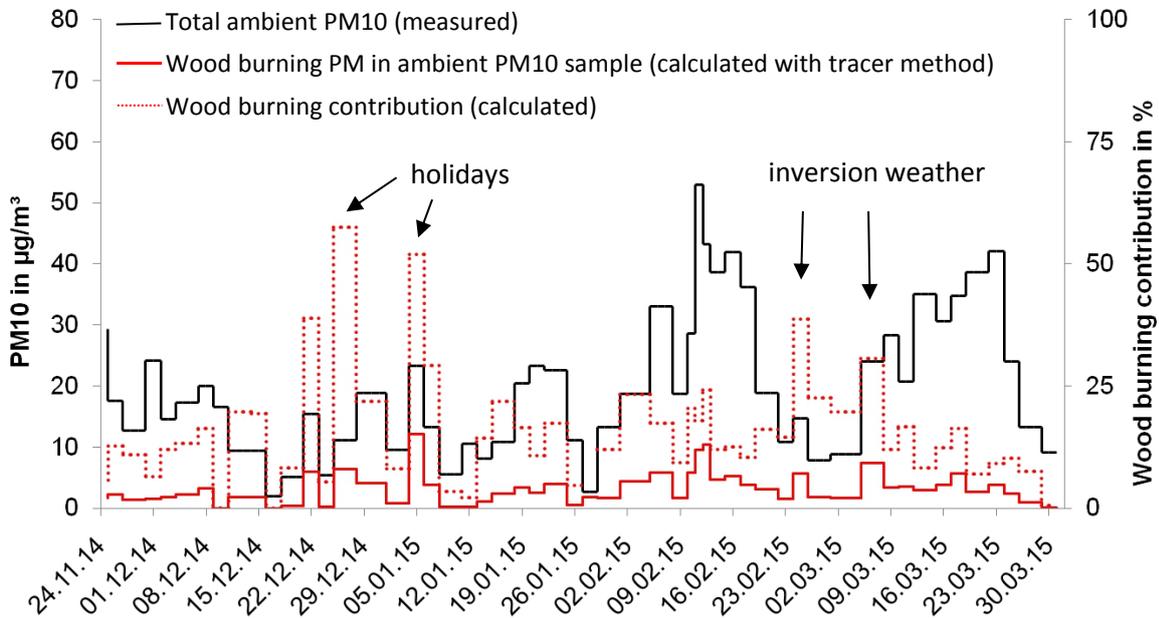


Figure 63: Temporal course of total ambient PM₁₀, wood burning PM and its contribution to total ambient PM₁₀ (calculated with conversion factor of 7.8)

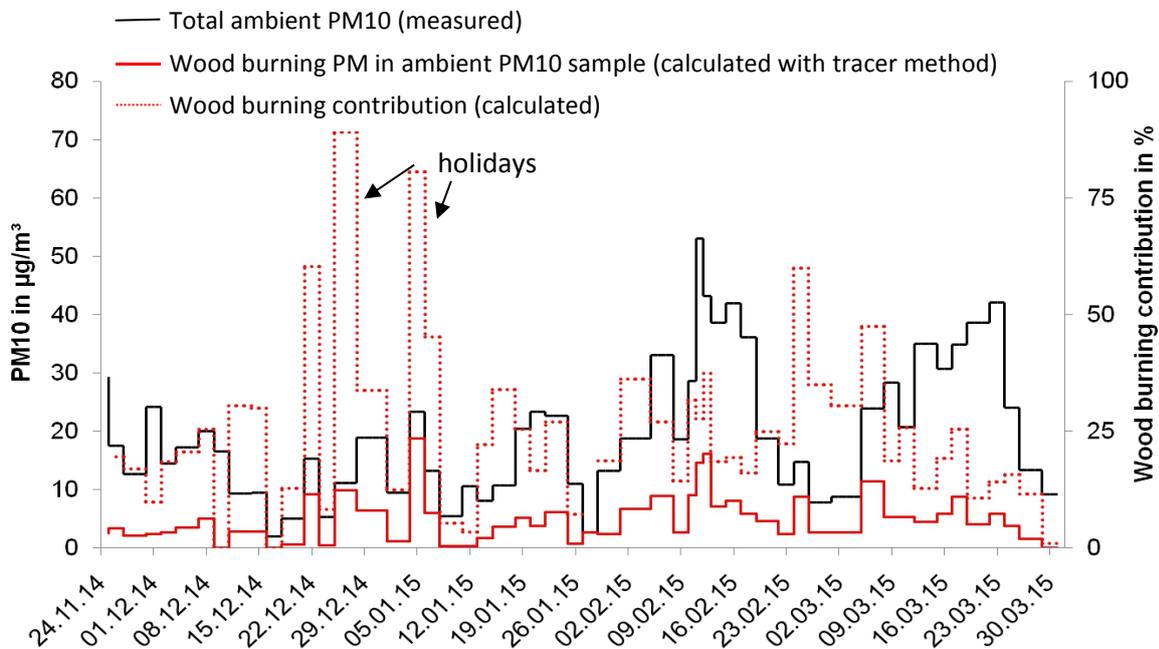


Figure 64: Temporal course of total ambient PM₁₀, wood burning PM and its contribution to total ambient PM₁₀ (calculated with a conversion factor of 12.1)

This wood burning contribution calculated with the levoglucosan conversion factor of 7.8 (see also Figure 63) is shown together with the result of biomass burning black carbon in Figure 65.

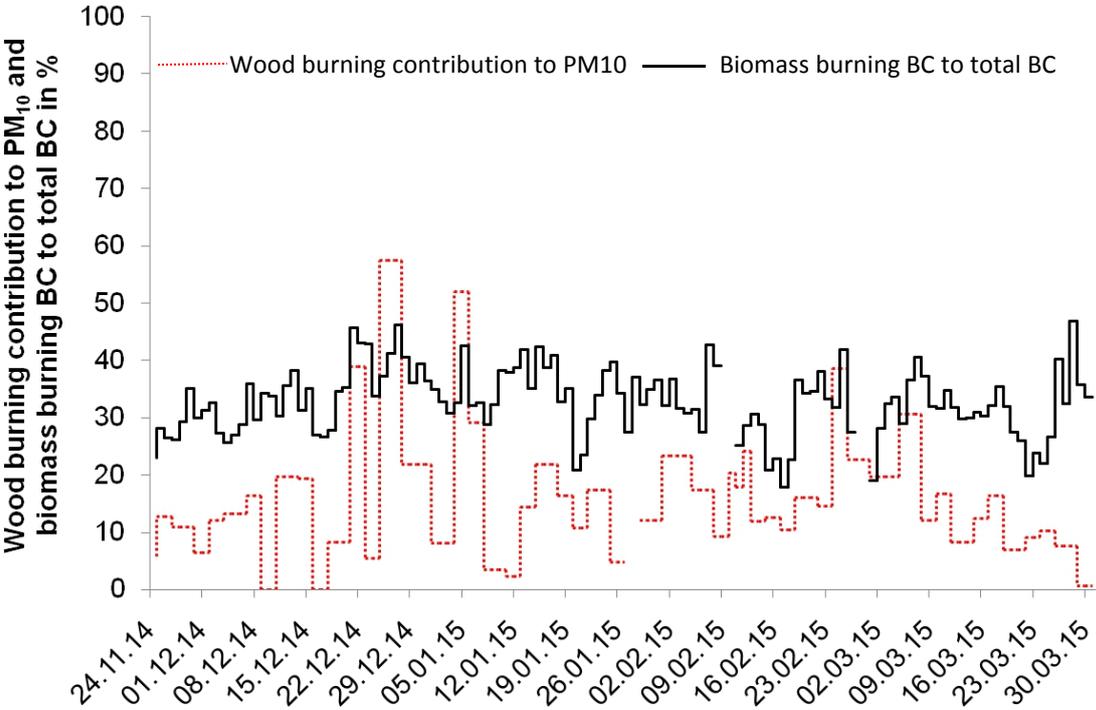


Figure 65: Biomass burning BC contribution (direct output from the Aethalometer) to total BC and wood burning contribution to total ambient PM₁₀ (calculated from the levoglucosan tracer method)

As introduced before, the source apportionment of black carbon could be directly attained by the output of the Aethalometer AE33 (Magee Scientific 2014) based on a mathematic model from Sandradewi et al. (2008b). This model realized in the software of the Aethalometer is able to deliver a direct output of the percentage of biomass burning BC to total BC (shown as BB%). The results from black carbon measurements are already shown in Figure 23 and Figure 24. The biomass burning black carbon presents significant portions of the total black carbon with an average value of 33.3 % (Figure 24).

It can be seen from Figure 65 that the biomass burning BC contribution to total BC has a similar trend to that of wood burning contribution to ambient PM₁₀ over the whole winter period, and high peaks from the two profiles agree with each other. That means that there is

relative high wood burning BC when there is a relative high wood burning PM₁₀. Both results prove the consistent wood burning effect on the local air quality. Meanwhile, biomass burning BC contribution to total BC is generally higher than the calculated wood burning contribution to total ambient PM₁₀ except those high contributions from holidays, indicating wood burning might has a larger effect on the local BC than on local PM₁₀. However, a direct comparison with the levoglucosan results is difficult since the black carbon particles (soot particles) are very small and therefore give a low percentage within the mass related PM₁₀. Further investigation including PM_{2.5} measurement would be necessary for a better comparison of the two parameters in Figure 65 .

The range of the conversion factor in this study is compared to some literature values which are also calculated from the levoglucosan tracer method. But only results in winter periods are shown and compared here even though some studies might have covered also summer time measurements. Therefore, some results are expressed in different ways (Table 24).

Table 24: Contributions of wood burning smoke to ambient PM₁₀ concentration in literature

Measurement Site and periods		Estimated contribution of wood smoke to PM ₁₀ or to OC		Used factor	Source
		To PM ₁₀ mass	To OC		
Austrian regions: Vienna, Graz and Salzburg (2004)	Background and residential areas	10 - 20 %	1/3 - 70 %	a	Caseiro et al., 2009
	Traffic-impacted areas	8 %	1/3		
7 sites (Urban-, sub-urban- and rural background) in Flanders, Belgium (2010 - 2011)		8.6 - 11.3 % Hamme: 22 %	36 - 43 % Hamme:22 %	a	Maenhaut et al., 2012
4 urban background sites in Flanders, Belgium (2011 - 2012)		6.5 - 9.8 %	34 - 41 %	a	Maenhaut et al., 2016
London winter 2010		8 - 10 %		b	Fuller et al., 2014
6 sites from the alpine valleys down to the rural sites in the plain: urban background in Lombardy (Northern Italy) (2005 - 2007)		5 - 25 %	20 - 50 %	c	Piazzalunga et al., 2011
		To PM₁₀			
4 urban background sites in Central and Northern European (2002 - 2003)		Prague: 37 % , Duisburg: 13 % Amsterdam: 11 % Helsinki: 17 %		d	Saarikoski et al., 2008
Helsinki Metropolitan Area (HMA) during 2005 - 2009 (PM _{2.5})		18 - 29 % (urban sites) 31 - 66 % (suburban)		e	Saarnio et al., 2012
7 measurement stations in Baden-Wuerttemberg (2015) (1) Near traffic stations (2) Urban background stations		Stuttgart Am Neckartor: 5 - 9 % Tübingen Muehlstrasse: 11 - 7 % Tübingen Jesinger Hauptstrasse: 20 - 32 % Stuttgart-Bad Cannstatt:11 - 18 % Gärtringen: 13 - 21 %		f	LUBW, 2016
Dettenhausen 2005 - 2006		36 %		g	Bari, 2009
Dettenhausen 2013 - 2015		16 - 25 %		h	This study

a: Factors of 6.1 and 10.7 for OC and PM₁₀, respectively (derived by Schmidl et al. (2008a))

b: Levoglucosan to PM emission ratio of 11 based on review from Puxbaum et al. (2007)

c: Weighted emission factors from literature data by the % of wood types in this region

d: MA-to-PM_{2.5} ratio of 0.12 from Fine et al. (2001, 2004)

e: Multiplying factor 24 derived from ambient-measurement with uncertainty of 9

f: Factors of 8 and 13 from literature

g: Using line regression of the ambient concentrations between levoglucosan and PM₁₀

h: Conversion factors of 7.8 and 12.1 derived from wood combustion experiments

Contributions of wood burning smoke to ambient PM₁₀ in the listed literature cover a relative wide range (from 5 to 66 %). Measurement sites with similar characterization show relative comparable results, for example, "Stuttgart am Neckartor" and a city area in Vienna are both traffic-impacted areas and have a contribution of wood smoke to PM₁₀ of ca. 8 %. The result of 16 to 25 % from this study is comparable to those measured in central and northern European urban background sites (Duisburg, Amsterdam and Helsinki), background and residential areas from three Austrian regions (Vienna, Graz and Salzburg), Sondrio in Lombardy and measurement stations from LUBW except station "Stuttgart am Neckartor". The contributions found in urban background from Flanders, Belgium and in London are somehow lower. This shows that wood smoke is a general pollution source in residential areas and in urban background across Europe. Bari (2009) calculated a contribution of 36 % for the same investigated area in winter 2005/2006, which is twice as high as the contribution calculated with the lower factor in this study and larger than all the other listed results except those from the suburban in Helsinki Metropolitan Area and stations in North Rhine-Westphalia. This high value is actually within the fluctuation range of this study (see Figure 63 and Figure 64). The high contributions found in this study indicate the serious wood smoke pollution, mostly happened during inversion periods. Since local emissions are dominant due to unfavorable dispersion conditions during an inversion, it is therefore to conclude that wood burning smoke is still a local pollution source especially in terms of PM in Dettenhausen. It can be concluded that wood burning contributes more in terms of BC than in terms of PM₁₀ if the local conversion factor of 7.8 is applied. A reduction of wood burning pollution is necessary for an improvement of the local air quality.

7. Summary, conclusions and outlook

The aim of this thesis is to quantify the wood burning contribution to ambient PM₁₀ during winter heating periods in a residential area in Dettenhausen, Germany. The air quality measurements in this area were first carried out by sampling ambient PM₁₀ and measuring gaseous pollutants (CO and NO_x) and black carbon in winter 2013/2014 and winter 2014/2015. The collected data are expected to reflect the realistic air pollution situation since the sampling site is near several buildings where people use wood burning for room heating. However, the contribution from residential wood burning to ambient PM₁₀ could not be quantified directly from these ambient data. According to the application principle and calculation procedure of the levoglucosan tracer method, the emission ratios of levoglucosan measured directly at an emission source are required. Therefore, wood combustion experiments at a wood stove were carried out for the sampling and investigation of PM-bound levoglucosan. The results of both ambient measurement campaigns and wood combustion experiments are summarized and concluded below.

7.1 Air quality in Dettenhausen in terms of PM₁₀, PAHs and BC

Mass concentrations of ambient PM₁₀ were determined from filter samples, which were subsequently chemically analyzed in laboratories for PM-bound polycyclic aromatic hydrocarbons and levoglucosan. The results show that the daily average concentrations of PM₁₀ during winter periods in this area are mostly below the EU daily limit value of 50 µg/m³. An overall average value of 20 µg/m³ is found for the two winter periods. However, the air quality is obviously deteriorated by wood smoke, especially, when inversion weather conditions occur. The PAH results have shown a relative high level of PAHs in ambient air, with an average value of 24 ng/m³ in January 2015, and the carcinogenic potential is 65 % of the total PAHs for both winter periods, with most of daily average benzo[a]pyren (BaP) exceeding the EU annual limit value of 1 ng/m³. Black carbon (BC) measurements with a continuous operating aethalometer show a daily average concentration of 1600 ng/m³

through winter 2014/2015 and very high concentrations up to almost 5000 ng/m³ are observed during inversion periods. The contribution of biomass burning BC to total BC is delivered directly by the aetholemeter with an average contribution of about 33 %. The PM pollution due to wood smoke could be also confirmed by the levoglucosan found in all PM filter samples. Levoglucosan was evaluated through its correlations with PM₁₀ and other pollutants like BaP, BC, and gaseous pollutants (CO and NO_x).

7.2 Emission behavior of levoglucosan at an emission source

For the investigation of levoglucosan in the flue gases from a wood stove, various parameters defined as "operation", "combustion" and "sampling conditions" were applied to investigate their potential influence on the levoglucosan emission levels. The experimental design included two sampling methods for beech hardwood and spruce softwood, which are commonly used for domestic heating in the residential area of Dettenhausen.

Levoglucosan sampling was performed first with simultaneous sampling of hot flue gas directly behind the stove and of diluted flue gas at the end of a dilution tunnel. The comparison of the results proves that a dilution tunnel is necessary to cool down and dilute the hot flue gas, enabling the condensation of levoglucosan on PM. The levoglucosan measured behind dilution should be used for the determination of emission ratios since it mimics the dilution and cool down process of hot flue gas in the ambient air. Therefore, levoglucosan was further investigated by sampling only behind dilution for different combustion phases.

The results of the experiments show that a large amount of levoglucosan is produced during the burn-up and the main-burning phase of hardwood burning. A high correlation between levoglucosan and volatile organic compounds (VOC) is found during the burn-up and the burn-out phase, which is consistent with the trend observed between odor and VOC in a previous project, indicating a high ratio of levoglucosan and odor appear together with VOC during the burn-up phase. Since VOC is a product of incomplete combustion, this correlation shows that levoglucosan is also emitted during incomplete combustion of wood.

Meanwhile, the cold-start mode affects significantly the emission, especially at the burn-up phase irrelevant of airflow setting regarding primary air and secondary air at the stove. Emission levels of levoglucosan from softwood combustion are much higher than those from hardwood combustion, which might be partially due to the lower temperature inside the combustion chamber during the softwood combustion.

The investigation of potential influences from various sampling conditions has shown that the dilution ratio could be controlled to be between 5 and 10, which corresponds to a sampling temperature of 35 ± 8 °C. Based on the emission levels of levoglucosan from three combustion phases, it is concluded that the sampling duration should cover both the burn-up phase and the main-burning phase. Thus, a 15-minute sampling is recommended, which would be sufficient for a rough estimation of the levoglucosan contents in PM emissions.

7.3 Estimation of wood burning contribution to ambient PM₁₀

By using levoglucosan as a wood burning tracer, the source apportionment of the total ambient PM₁₀ was carried out. The emission ratios of levoglucosan of both hardwood and softwood were first calculated. Together with different assumptions for the local wood consumption structure, local conversion factors were calculated for the investigated area. Two assumed hardwood shares of the total wood consumption, which are 85 % and 95 %, are considered as very close to the real local situation. The conversion factors calculated from these two shares, which are 7.8 and 12.1, respectively, are chosen for the estimation of wood burning contribution to ambient PM₁₀.

With this tracer method, for winter 2014/2015, an average concentration of wood burning PM is calculated as 3.0 ± 2.4 µg/m³ with a conversion factor of 7.8 and as 4.7 ± 3.7 µg/m³ with a conversion factor of 12.1 in this area. The corresponding wood burning contributions to the total ambient PM₁₀ are 16 % and 25%, respectively. Both the two chosen conversion factors and the calculated contributions are comparable to results from similar studies relating the wood burning contribution in urban background areas across central Europe. A previous study in this area has calculated a twice larger contribution (Bari et al., 2010),

which is comparable to the high contributions during inversion weather conditions in this study. Both the calculated wood burning contribution to ambient PM₁₀ and the contribution of biomass burning black carbon to total black carbon show that wood smoke PM from residential wood burning pollutes the local air during the winter heating periods especially under inversion weather conditions. Therefore, measures should be taken to reduce PM emissions from residential wood burning.

The results of levoglucosan and black carbon in this study show that incomplete combustion causes wood burning smoke as part of the ambient PM₁₀ in this residential area. Therefore, burn-up phase from cold-start wood combustion in chimney stoves and manual fed log wood boiler should be reduced. The up and down of the combustion during manual feeding can be reduced by modern technology with boilers which have a downwards flame independently from the filling of the furnace and a controlled combustion. Another possibility to reduce wood smoke emissions is the usage of wood pellets as fuel which has a continuous combustion avoiding the regular emission-relevant burn-up phase.

7.4 Future work direction

With regard to the ambient study, winter measurement of air pollutants in the investigated area should be continued with focus on PM₁₀, PM_{2.5} and black carbon. More PM samples should be analyzed for organic carbon and elemental carbon content for a better analysis of their sources. The study of levoglucosan direct at an emission source in this study could be further developed in several aspects. First, more sampling repetitions for each experiment setting should be carried out to get a better average value of levoglucosan emission ratio. Secondly in order to further understand the possible influence of various factors on levoglucosan emission, different kinds of combustion units with different combustion behavior should be tested, for example, investigation of the emissions from residential oil burning at an emission source, since this is the dominant heating method in this residential area. These data could be applied for modeling the PM dispersion and for inventorying pollutant emissions.

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